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SOIL SCIENCE

Contents for April, 1920

(4) BRIGGS, ... , AND ...
Danish Agric. Plant. Serie 98, p. 85.
(5) BRIGGS, ... , AND McLAREN, J. W., 1940, ... centrals of determina...
... implication... of ... ... v. ... p. 135 ...
... AND SHAW, ... , 1950, ... coefficient of diffe...
... its induce... of ... ...
... ...

REDUCTION POTENTIALS OF BACTERIAL CULTURES AND OF WATER-LOGGED SOILS

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The importance of oxidational processes in soils is attested by a voluminous literature, and has been emphasized and studied from various angles in publications from this laboratory by Oswald Schreiner and collaborators (31, 33, 34, 36, 37). A review of the literature and a broad discussion of the subject have been given in these publications (especially 31, 33). By the use of chemical tests it has been found that soils are often oxidizing, and it has been concluded that, as a rule, good "vital" soils are more so than poor soils. It has also been suggested that it is possible for a soil to be too oxidizing (34), though there is not yet a satisfactory way of determining by laboratory examination when such a condition exists. There is also a considerable literature on oxidation and reduction by yeasts and bacteria, which has not yielded the fundamental results which may be eventually expected. Reduction processes in soil have also been studied, though to a lesser extent (18, 36).

Just as a sharp line can be drawn between acidity and alkalinity, taking the reaction of pure water as the standard, so can a sharp line be drawn theoretically between oxidation and reduction, taking as a standard the properties of pure water (39). The parallelism goes a long way. Both acidity and oxidation are relative terms and such absolute theoretical distinctions are of limited significance. A neutral condition is not necessarily the optimal condition for soils, in fact is not acid enough for certain systems of cropping (13), and the theoretical point between oxidation and reduction is probably not the best condition for soils. Differences in acid intensity have been studied of late in soils by the use of an electrode saturated with hydrogen gas at the atmospheric pressure. Let us consider differences in intensity of oxidation and reduction, as studied by means of an electrode of noble metal, upon which no pressure of hydrogen or oxygen is purposely applied.

Energy in its various forms has two factors, intensity and quantity. This is true not only of energy in the usual physical sense, but also in a very broad sense, including the energy of acidity (of which the two factors may be taken as hydrogen-ion exponent[1] and quantity of acid) and the energy of oxidation

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[1] Dr. E. Q. Adams pointed out to the writer that the hydrogen-ion exponent, rather than the concentration, is the true intensity factor of acidic energy, in properly chosen units.

199

and reduction. In various studies on oxidation and reduction in soils only the quantity factor has been studied, such as the oxygen consumed or the carbon dioxide given off, or the quantity of colored substance produced by the action of soil on a given suitable reagent. Other things being equal, the intensity factor might be assumed to vary in parallel with the quantity factor, but unfortunately this assumption is very doubtful when different soils are being compared.[2]

In the case of oxidation and reduction, the so-called oxidation or reduction potential represents the intensity factor. This potential is the electrical potential difference between a solution and a chemically indifferent electrode immersed in it. If two such electrodes are set up, immersed in two liquids of different oxidation potential, the liquids being connected by a siphon, then on making metallic electrical connection between the electrodes a current will pass, and oxidation of the solution about one electrode will occur and reduction of the solution about the other.[3] Which solution is oxidized at the expense of the other will depend upon which oxidation potential is the greater, and if the two potentials happen to be the same no current will pass and no chemical action take place. In general, the magnitude of the potential difference between the two electrodes gives no information as to the quantity of current which can be obtained from the system, and in many cases very little current can be taken without lowering excessively the potential difference. It will be observed that oxidation and reduction potentials always occur in pairs, there being apparently no certain way of obtaining a single potential with any accuracy. However, cells may be set up in which there is only one variable half-cell, in which case we may treat the total electromotive force as the oxidation or reduction potential, taking for purposes of comparison the constant half-cell as a zero. A calomel electrode is generally taken as the constant half-cell, and its potential is sometimes taken as zero, sometimes as some other more or less arbitrary number. By referring the oxidation potential of a variety of oxidizing and reducing agents to a calomel electrode for comparison, Neumann (23) was able to arrange the various agents in a continuous series, using largely the measurements given by Bancroft (2). It is well known that this cannot generally be done by chemical means, and it unfortunately follows that such electrical measurements do not always predict successfully the chemical behavior of two given solutions when they are *mixed*. The results may of course depend on reactions of different type, especially upon catalytic actions. The significance of the electric potential

[2] Suppose a certain soil is found to absorb oxygen at a higher rate than another soil, and so may be properly said to respire with greater intensity; this fact does not show whether the soil contains very easily oxidizable bodies, for it may contain instead a large quantity of less easily oxidizable bodies. A study of the intensity factor would be necessary for such a distinction.

[3] It is to be understood that oxidation and reduction are taken here in the broad sense, referring either to the participation of oxygen or hydrogen or to a mere change of valence.

in chemical reactions is discussed at length in Chapters XIV and XV of Stieglitz's *Qualitative Analysis* (35).

By comparing the oxidation potential of oxygen in solutions of various alkalinity with that of various mixtures of potassium ferro- and ferricyanide solutions (the potentials of which are practically unaffected by changes of reaction if substantial quantities of both forms are present), Fredenhagen (11) was able to show that there was a particular ratio of ferro- to ferricyanide which was stable at a definite alkalinity. At greater hydrogen-ion concentrations the proportion of ferricyanide in the mixture would be greater, for equilibrium with oxygen. In the soil, the oxidizing potential of oxygen (at a pressure of 0.2 atmosphere) would also be greater under acid conditions, and oxidations in acid soil should therefore on the whole go further than in neutral or alkaline soil. In bacterial cultures or in water-logged soil the hydrogen-ion concentration establishes a limit of reduction potential (the potential of the hydrogen electrode gives this limit), which cannot be greatly exceeded without the liberation of hydrogen gas.[4]

It is obvious that measurements of hydroxyl-ion or hydrogen-ion concentration are necessary for the fullest interpretation of oxidation or reduction potentials. Wells (39) and Frary and Nietz (9) have recently made use of such hydrogen-ion concentration data in the interpretation of oxidation potentials. It is doubtful, however, whether all interpretation of oxidation potential must be made in this way. The Nernst theory, that oxidation and reduction potentials are due to charges of oxygen or hydrogen gas (or of both, in equilibrium), has been vigorously disputed by van Laar (38), who says that in many cases such gas charges are fictitious. The fundamental thing which determines the occurrence of oxidational reactions in electric cells is not the pressure of oxygen or hydrogen gas, but is the actual potential itself, and the writer has therefore preferred not to "correct" such potentials by means of the hydrogen-electrode potentials, except in special cases, where an equilibrium involving gaseous hydrogen seemed to exist.

TECHNICAL DISCUSSION

Solutions differ in their action on an indifferent electrode; in some, like mixtures of potassium ferro- and ferricyanides, the electrode exhibits quickly a constant and reproducible potential (20), whereas in others, such as photographic developers (9) the potential varies for weeks. In the latter case it may often be difficult to show that the potential measurements have much significance. If the potential is the result of an equilibrium between one substance and its immediate oxidation or reduction product, and both substances are present in fair concentrations, then, as Peters showed for various salts of iron (26), constant and reproducible potentials are exhibited, the

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[4] Unless the phenomenon of overvoltage is possible in these cases. No such phenomenon was met in this work. It might perhaps be expected in media rich in sulfur.

potential can be calculated by van't Hoff's equation from the concentrations of the substances involved, and the potentials have therefore a definite chemical meaning. In cases where the potentials are inconstant, even if they are simply keeping pace with a progressive chemical reaction, it is difficult to establish the chemical significance. The tendency of a chemist is therefore to avoid the study of systems which do not give constant potentials, but a progressive variation of potential in a biological system such as soil should not deter the investigator, because biological significance may be capable of demonstration, even if chemical significance may not.

The definiteness of the intensity factor in oxidation is dependent to some extent upon the magnitude of the quantity factor. The situation is similar with regard to acidic energy. The behavior of a hydrogen electrode is unsatisfactory in solutions having minimal "buffer action," and we may speak of the ferro-ferricyanide mixtures as being well provided with *oxidative buffer* properties. The usual term "buffer action" may be distinguished when necessary by the qualification *reaction buffer*. Soils, as well as bacterial cultures, show little oxidative buffer as compared with ferro-ferricyanide mixtures, and this is the cause of a fundamental difficulty in soil work. Because of this it is necessary to add water to the soil in which an electrode is immersed in order both to secure good electric contact between the soil and the electrode and also to exclude air, for the oxygen of the air goes into quick reaction with the electrode, disturbing the potential and making it uninterpretable. It is therefore somewhat difficult in such cases to assume any significance to potentials unless they are definitely different from the potentials which atmospheric oxygen would impart, because if oxygen values are seen, it may be objected that they are due merely to oxygen carried on the surface of the electrode or dissolved in the soil, the soil itself being inert. It is because of this difficulty that the soil work reported in this paper is confined to water-logged soils. It may, however, be perfectly possible in some cases to obtain significant potentials a short time after wetting the soil and introducing the electrode.

All the "potentials" recorded are the electromotive forces of the entire cell, including the saturated potassium chloride calomel electrode. In most cases the positive terminal of the cell was the mercury of the calomel electrode (as is the case in ordinary hydrogen electrode measurements) and in these cases the potential was recorded positive, so that high positive values represent a high intensity of reduction, and high negative values would represent high intensities of oxidation. The sign, therefore, refers to the solution in all cases, and not to the electrode immersed in it (which of course has the opposite sign). It was until lately the practice to correct the observed potential differences for an assumed value for the single potential of the calomel half-cell, taking the 1 N KCl calomel electrode potential equal to 0.56 volts, the mercury being positive to the potassium chloride solution. This assumption is equivalent within 0.01 volt to taking the 0.1 N KCl calomel elec-

trode potential as equal to 0.62, and the saturated KCl calomel used for these measurements as equal to 0.53, at the ordinary temperatures (20–30°C.). In these cases also the mercury is positive. If therefore we correct our observed potentials by subtracting 0.53, the results will be comparable with the table of "absolute potentials" of Neumann (23, p. 228), and of van Laar (38), in which the single potentials refer to the potential of the *solution* against the electrode immersed in it; but if we wish to compare them with the absolute potentials given by Wells (39), we must subtract 0.53 and then change the sign of the result, for in his table the single potentials refer to the potential of the *electrode* against the solution. The potential of the normal hydrogen electrode is of late taken as an arbitrary zero, which gives 0.283 instead of 0.56 for the 1 N electrode, and therefore 0.25 instead of 0.53 for the saturated electrode used. At present it seems well to present the potentials uncorrected. If, during any measurement, the saturated electrode had been removed and a 1 N electrode substituted, the fluid or soil would have appeared to be about 0.03 volt more reducing.

All of the experiments except the last soil experiment were done in 1915, and the potentials were then measured by means of the voltmeter scheme given by Hildebrand (15) with the use of a capillary electrometer. The voltmeter readings were 1.5 per cent too high (after the zero position of the needle was adjusted) and this correction (determined at the time with the kind cooperation of Dr. W. Mansfield Clark) was applied. For the other experiment a good potentiometer was used with a galvanometer, the coil of which has a resistance of about 400 ohms.[5]

Various metals have been used for the unattackable electrode. Platinum has been used either blank, or made gray (2) by coating with platinum black and heating in the flame. Mercury has been used, for solutions not so oxidizing as to act on the mercury, producing a calomel electrode (7, 8). Gold has been especially recommended by Lewis and Sargent (20); gold elec-

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[5] A voltmeter reading directly to 20 millivolts (0.020 volts) is fairly satisfactory even for much hydrogen electrode work, if calibrated, and if tenths of a division can be accurately estimated.   The homemade capillary electrometer used (Ostwald form) was more satisfactory than the voltmeter.   Not too fine capillary tubing was used.   It was sensitive to about 0.0005 volt, applied across the terminals, and in series with a gas chain of high resistance it was still possible to read to 0.001 volt; whereas a good galvanometer, unless its coil has a high resistance (say 400 ohms), may fall far behind a capillary electrometer if used in a high-resistance circuit.   It is necessary to maintain the short-circuit (except at the moment of use) through secure connections (platinum contacts, well-soldered connections, or freshly-applied pressure by screws).   It was seldom necessary to blow over a drop of mercury, as care was taken not to hold down the key long enough to overcharge the electrometer.   The surface of the mercury can be put in good condition, when necessary, by applying an electromotive force about 0.8 volt, connecting the capillary pole with the negative lead (so that the mercury contracts in the capillary) and then letting stand 15 to 30 minutes short-circuited (25).   Simple electrical shielding (40) was found to prevent the trouble otherwise experienced with the capillary electrometer outfit in damp weather.

trodes were found sensitive to light by Bose and Kochan (3), a matter of 0.1 volt. The writer has not used gold, and has not seen any certain light effects; light, however, was excluded to a reasonable degree in all the measurements reported.

REDUCTION POTENTIALS OF MICROBIAL CULTURES

Potter (27, 28) measured the electromotive force produced when two platinum electrodes were placed in two portions of culture medium, separated by a porous partition, and one portion was inoculated with yeast or *Bacillus coli*. In both cases the electrode in the inoculated portion was more zincative (negative) than the uninoculated portion. Glucose medium was used for yeast, and a synthetic medium containing ammonium tartrate, asparagin, and mineral salts for *B. coli*, also for the latter organism a medium with starch substituted for the asparagin. The maximum electromotive forces developed were 0.3 to 0.4 volt, and in the last case 0.5 volt. He did not interpret these results in terms of oxidation or reduction, in fact stated that no electric effects could be produced by oxidation of the platinum electrodes, but spoke of the liberation of electrons of the organic substance during the decomposition and of the electrical charges set free in the vital processes of the microorganisms. The difference of interpretation, however, is chiefly a matter of language alone. The direction of the electromotive forces described is such as to point to the establishment of reducing conditions by the microbial activity. No potentials against a calomel electrode were measured. Varying the concentration of yeast, Potter found the maximal electromotive force to be developed more quickly, the more concentrated the yeast suspension.

Mixed culture, mercury electrode

A considerable number of experiments were made by the writer using a mercury electrode, of which only a few will be given. The electrode vessel was the glass part of an ordinary spirit lamp. By means of appropriate glass connections the electrode vessel could be completely filled with mercury, displacing all air in the vessel and in the tube used for filling. This tube was long enough to reach to the bottom of the cultures examined. Stopcocks made it possible to make a liquid contact with saturated potassium chloride solution leading to the calomel electrode, and by admitting more mercury an old contact could be forced out and a new one made at any time. The vessel could be gently shaken to aid the attainment of equilibrium. This arrangement was used to examine bacterial cultures, and gave good results in the examination of mixed cultures grown in deep layers when care was taken to avoid the entrance of air. Such cultures were carefully protected against agitation. Though no test was made, the cultures undoubtedly contained anaerobes. If air was purposely or accidentally admitted to the

cultures, the potentials were disturbed and sometimes a prohibitive length of time was required to re-establish equilibrium. Figure 1 shows the time curves for a mixed culture in a deep layer of 1 per cent Witte peptone. This culture was obtained by inoculation with soil one month previously, and had stood a number of weeks without agitation before it was introduced into the electrode vessel. In figure 1, curve A shows the change of potential with time when the culture was introduced with care to avoid entrance of air, curve B shows the relation for the same culture when a little air accidentally gained access, and curve C shows the relation when the culture was shaken with air. By admitting air in small quantity to the culture in the electrode vessel it was possible to disturb the potential in less degree, and in this case the potential was observed to return to the former value in a few hours. Attempts to displace the equilibrium in the opposite direction by passing in hydrogen gas failed. The culture was nearly neutral to litmus paper.
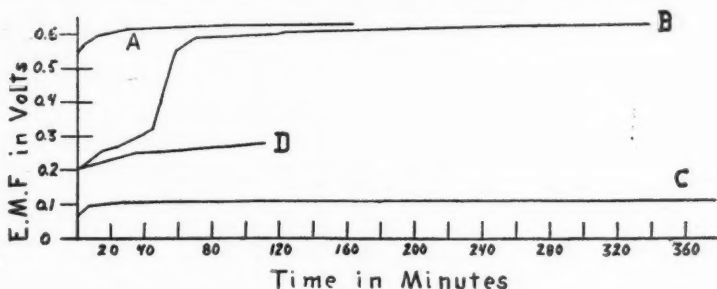

FIG. 1. REDUCTION POTENTIALS OF BACTERIAL CULTURES

A similar culture 17 days old was tested in the same apparatus with careful exclusion of air and in addition the hydrogen electrode potential was determined. Constant potentials were found, 0.630 and 0.707, for the mercury and hydrogen electrodes, respectively.

A similar culture 20 days old, grown in a different vessel, gave in the same apparatus the following constant potentials for the mercury and hydrogen electrode potentials, respectively: 0.616 and 0.715.

In these cases a little time was required for the reduction potential to become constant, as in the case of the experiment plotted in figure 1. The final values for the reduction potential were in fair agreement, being 0.620, 0.630, and 0.616, under conditions not exactly the same.

Bacillus subtilis, amalgam electrode

A sheet of platinum about 1 by 3 inches, provided with a platinum wire connection sealed through a glass joint, was rolled into a hollow cylinder and amalgamated by immersion in boiling mercury. It was introduced by means

of the glass joint into a test-tube, to the bottom of which was sealed a T-form double stopcock. One arm of the stopcock was used as a pipette for filling and the other for making liquid contact with saturated potassium chloride solution (which was connected with the calomel electrode). An old culture (one month) of *Bacillus subtilis* on 1 per cent Witte peptone, the growth of which had sunk to the bottom, was introduced to the electrode vessel, completely filling it to the exclusion of air. The observed potential was 0.19, rising to 0.26 in 30 minutes. By means of an auxiliary electrode (replacing the calomel electrode) the reduction electrode was polarized until its potential (measured against the original unpolarized calomel electrode) was 0.314. On standing, the potential returned in an hour to the value 0.23, showing that this value represented an equilibrium, if only a temporary one. The hydrogen electrode potential was 0.753.
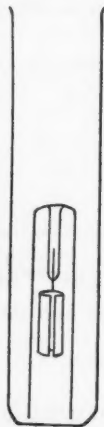
FIG. 2. "INVERTED-VIAL ELECTRODE"

Another experiment was performed with the same amalgamated electrode. A 3-day culture of *B. subtilis* was used; the culture having been grown on a mixture of Witte peptone 1 per cent, dextrose 1, and K_2HPO_4 0.5 per cent. The reduction potentials are shown in figure 1, curve *D*. The highest reached was 0.275; the hydrogen-electrode potential was found to be 0.622.

Bacillus coli in inverted vial electrode

B. coli was grown in an "inverted vial" provided with a bare platinum electrode, as shown in figure 2. After the growth, mercury could be introduced into the tube carrying the platinum wire, for metallic connection with a copper wire leading to the voltmeter arrangement. Two cultures of *B. coli* were obtained through the kindness of Dr. W. M. Clark. They had been found to be typical cultures, with a gas-ratio, $CO_2:H_2$, nearly equal to 1, as determined by exact analysis over mercury (29). The reduc-

tion potential was measured before the bubble of gas touched any part of the platinum. The sheet of platinum was about 1 inch square. The culture medium was Witte peptone 1 per cent, dextrose 1, and K_2HPO_4 0.5 per cent. Liquid contact was made by means of a capillary tube filled with saturated potassium chloride solution, which was dipped to the bottom of the tube with as little agitation as possible. The temperature was about 25°C. The hydrogen electrode potentials of both cultures were also measured. All potentials, reduction and hydrogen, appeared quite constant. From the reduction and the hydrogen potentials the pressure of gaseous hydrogen was calculated from the equation: $\log pH_2 = -33.8E$, where pH_2 is the pressure in atmospheres of gaseous hydrogen, E is the difference in volts between the hydrogen and reduction electrode potentials, and 33.8 is the reciprocal of the familiar factor $RT/2F$ after correction for conversion of logarithms.[6] The results are shown in table 1.

TABLE 1

Reduction and hydrogen electrode potentials of two cultures of B. coli, and the pressures of gaseous hydrogen calculated therefrom

CULTURE	OP	HX
Reduction potential (volts)	0.580	0.516
Hydrogen potential (volts)	0.594	0.554
E (volts)	0.014	0.038
Value of log pH₂	−0.473	−1.282
Log pH₂	$\bar{1}.527$	$\bar{2}.718$
Pressure of hydrogen gas (pH₂) (atmospheres)	0.34	0.052

It is not supposed that such gas analysis is accurate, but the fact is of interest that the potential of bare platinum pointed to concentrations of hydrogen gas of the order of magnitude that would be expected. For the ratio, $CO_2 : H_2$, equal to 1, the pressure of hydrogen would be 0.5 atmosphere, calling for a difference of about 0.009 volt between the reduction and hydrogen-electrode potentials. From table 1 it is seen that the calculated pressures were 0.34 and 0.052. These values are less than that established by exact analysis of the gas obtained by growing the organism *in vacuo*, but if oxygen is not excluded the analysis also shows smaller proportions of hydrogen gas (17).

[6] This equation represents the relation between two hydrogen electrodes at different hydrogen gas pressures (one atmospheric pressure, and the other, to be determined), immersed in a solution of one hydrogen-ion concentration; and can be obtained, for instance, from an equation given by Wells (39), second equation on page 58, by applying this equation for the single potential to the case where the pressure of hydrogen gas is 1, when the log term becomes 0, and then to the case where the pressure is pH_2, and finally subtracting one result from the other. This equation then applies not only to a neutral solution, but to any other, since the equation from which it was derived is affected by changes in reaction only in the term −0.136 (the minus sign was omitted in the bulletin through a printer's error), which disappears in the subtraction, whatever its value may be at the particular hydrogen-ion concentration.

Reduction potentials of bacterial suspensions

Thick suspensions of bacteria produce reduction of methylene blue far more quickly than cultures, or thin suspensions. Such suspensions have been used in studies of bacterial reduction of colored substances (5, 14, 24).[7] *B. coli* "hx" was suspended in 0.9 per cent sodium chloride solution with the addition of a little broth, and measured in an apparatus similar to the amalgamated electrode vessel, but the electrode itself was bare platinum, not amalgamated. The temperature was 26°C. The progress of the experiment can be seen from figure 3. The maximal reduction potential was 0.599 volts, decreasing to 0.594, doubtless because of acid formation, as the hydrogen electrode potential, subsequently determined, was 594, decreasing to
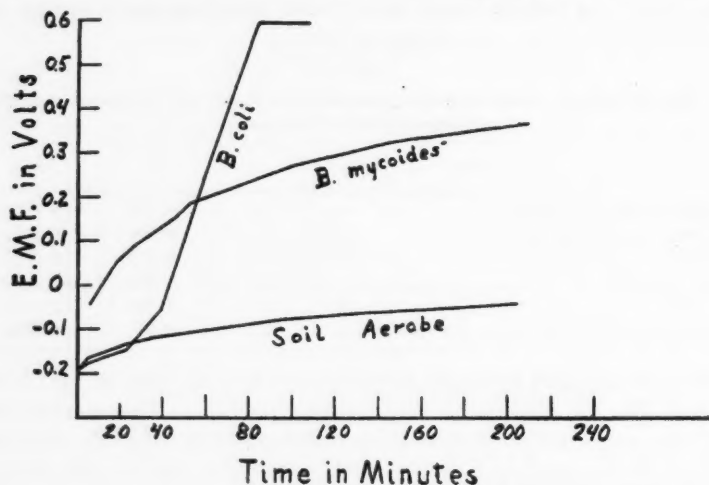

FIG. 3. REDUCTION POTENTIALS OF BACTERIAL SUSPENSIONS

592. Thus the two potentials were very nearly the same. *Bacillus mycoides* was grown on agar and suspended in broth. It was studied in the amalgam electrode, and the results are shown in figure 3. The highest reduction po-

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[7] To the data of Harden and Zilva may be added the following facts, determined by the writer in 1910 but not published. When masses of *B. coli* were washed so that on the addition of methylene blue solution alone no reduction could be seen on incubation at 37°, and the effect of various substances on the reduction was examined, dextrose and glycerol were found to be active in especially small concentrations. At least as small concentrations as 0.02 and 0.002 per cent, respectively, caused the reduction of the methylene blue to take place. Traces of ammonium hydroxide were also very active, and this seemed to make tests of the activity of the sodium salts of weak organic acids uninterpretable without hydrogen-ion control. Dextrose and glycerol were found by Cole (5) to be very effective also in aiding the formation of methemoglobin from hemoglobin by the action of pneumococcus suspensions.

tential was 0.37; whereas the hydrogen electrode potential was 0.700.   An unidentified soil aerobe, motile, liquifier of gelatine, not identical with *B. mycoides* or *B. subtilis*, was grown on agar, the growth suspended in a mixture of equal parts of 0.1 *M* Na_2HPO_4 and 0.1 *M* NaH_2PO_4, and examined with a gray platinum electrode.   In this, as in all these cases, the electrode vessel was of course completely filled with the suspension, to the exclusion of air.   The highest reduction potential was -0.04, whereas the hydrogen-electrode potential was 0.652.   The intensity of reduction was therefore very low in comparison with the other cultures, but this culture gave a good indophenol test with Ehrlich's reduction reagent (6), a mixture of para-nitrosodimethyl anilin and alpha-naphthol.

REDUCTION POTENTIALS OF WATER-LOGGED SOILS

Hagerstown loam

Two hundred grams of soil, stated to be Hagerstown loam, were placed in a tumbler and enough water added to saturate the soil and make a thin

TABLE 2

Reduction-potential experiment with Hagerstown loam plus dextrose

DEXTROSE		REDUCTION POTENTIALS AFTER VARIOUS PERIODS			
		1 day	2 days	3 days	4 days
gm.	*per cent*				
0	0	-0.32	-0.16	$+0.07$	$+0.11$
0.25	0.125	-0.18	$+0.44$	0.32	0.26
0.50	0.250	-0.24	$+0.44$	0.31	0.31
1.00	0.500	-0.32	$+0.46$	0.48	0.45
2.00	1.000	-0.02	$+0.48$	0.52	0.50

layer of water over the top.   Similar tumblers were prepared, using the same soil to which dextrose had been added before wetting.   Gray platinum electrodes about 1 inch square, attached to platinum wires sealed into glass, were introduced by opening the soil with a knife, the soil was pressed back, and the whole allowed to stand.   At daily intervals, liquid contact with the saturated potassium chloride solution was made by laying a capillary tube filled with the potassium chloride solution on the soil, and the potential against the calomel electrode was measured.   After each measurement the capillary tube was removed, and the soil which was contaminated with potassium chloride was scraped out.   The reduction potentials are given in table 2.

Some of the irregularities may be due to the fact that the layer of water evaporated, leaving in some cases fine cracks which permitted air to gain entrance to the layers of soil near the electrode.   The layer was restored by daily addition of water.   It is noteworthy that the smallest quantity of dextrose added to the soil, about 0.1 per cent, produced a very large effect on the soil after water-logging for two days.

Duplicate tumblers were prepared and young rice seedlings were replanted in the water-logged soil, the soil being kept just wet. In 2 days, differences could be seen, and in 3 days the rice seedlings were apparently normal in the water-logged soil containing no dextrose, but were progressively poorer in the soils to which dextrose had been added. The injurious effect was definite with only 0.125 per cent of dextrose, and the plants were in very bad condition with the higher concentrations. The experiment with rice is only suggestive, as a number of factors were not studied. It was not known at the time how to measure the hydrogen-ion concentration of soils.

A less extensive experiment showed that Witte peptone added to the same soil produced reducing conditions, when the soil was water-logged, but the effect was not so marked as in the case of dextrose.
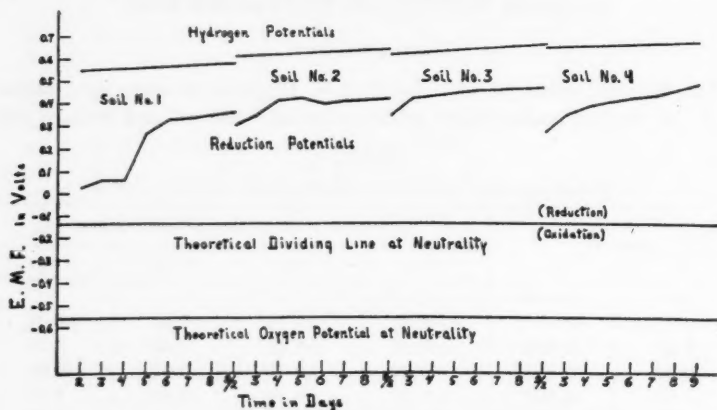

FIG. 4. REDUCTION POTENTIALS OF WATER-LOGGED SOILS AT VARIOUS TIMES

Various soils without dextrose

As electrode vessel, a tube was used open at both ends. A platinum electrode coated with palladium black, sealed into a glass tube, was carried on a rubber stopper fitting into the tube. The electrodes were much smaller than those used previously, being only 3 or 4 mm. square, and were treated as for a measurement of hydrogen-ion concentration, but were well exposed to moist air before use, in order to permit the removal of hydrogen which had been deposited in the sulfuric acid "cleaning" bath. The tube was filled as tightly as possible with wet soil, using as thick a mud as could be handled without inclusion of air. After filling the tube, the end was closed with thin rubber sheeting, secured with rubber bands. Each day the rubber sheet was removed, contact made with a rubber tube containing saturated potassium chloride solution, and the potential measured. After the measurement the contaminated soil was at once scraped out and replaced with fresh soil,

without disturbing the layers of soil about the electrode, and the rubber sheet replaced.

Four soils were studied.   No. 1 was Caribou loam; no. 4, Washburn loam, the others being soils from another region.   In figure 4, the reduction potentials thus measured are shown, as curved lines.   The straight, slanted lines show the hydrogen electrode potentials for the soils, determined without water-logging, and at the end of the period of water-logging, in each case. For purposes of illustration, the theoretical line dividing oxidizing from reducing solutions at the hydrogen-ion exponent 7, has been shown, as well as the potential which an oxygen electrode would show (19) at the same hydrogen-ion exponent if the experiment could be correctly performed.   The hydrogen electrode potential line for the exponent 7 has not been drawn, since it is so near the slanting lines as to produce confusion.

There appears to be a significant difference between the Caribou loam (no. 1) and the other soils, as water-logging produces a much slower effect with it than with the others.   To make sure of this point the whole experiment was repeated, using the same electrodes as before, but without recoating, or even cleaning beyond simple rinsing, and the electrodes were interchanged, so that no soil was tested with the same electrode again.   The results were very similar, the main difference being that the rate of production of reducing conditions was different, presumably because of a change of room temperature.

SOURNESS OF SOILS VS. ACIDITY OF SOILS

A few years ago an anomalous situation existed with regard to soil acidity. It was held by many that the reaction of ordinary soils was either neutral or slightly alkaline, reactions with blue litmus paper notwithstanding.   The reddening effect of certain soils upon blue litmus paper was held to be due solely to adsorption.   At the same time many investigators were applying litmus paper to detect soil acidity and recommending its use to the farmer, holding to the point of view that although soil acidity may not be proved by the use of litmus paper, the reddening effect on blue litmus paper is often correlated with the failure of red clover and other crops supposedly intolerant of acid conditions.   By such investigators the word "acidity" was applied to soil problems with due regard to the opinions then current and quotation marks about the words "soil acidity" and various qualifying phrases were often used in order to waive the question as to whether a "true" acidity was involved.   The acidity or sourness of soils could not be measured by any one method which would indicate whether an injurious degree of acidity was in question, and it resulted that soil acidity became a broad biological concept, rather than a definite chemical one, and was judged in various ways; principally from consideration of (a) the effect of the soil on vegetation, (b) the effect of the soil on litmus paper, and (c) the drainage.   It was com-

monly assumed that poor drainage was associated wtih an injurious degree of "acidity." It is true that a correlation has sometimes been found between poor drainage and high lime requirement; it is also true that in the experience of this laboratory the better drained soils have a higher hydrogen-ion concentration (a lower exponent) than the correlated, more poorly drained soils. To the mind of the writer it is very questionable whether the injurious effects of poor drainage on vegetation are in fact usually due to a high degree of acidity. It seems very probable that what is often called *sourness of soils* consists sometimes of a very *real* (i.e., injurious) acidity, but sometimes, namely when it is a case of poor drainage, of another property of soils, as yet not understood. Though at present it cannot be demonstrated, it seems more than likely that this other property of badly drained soils is their reducing power, and furthermore that the intensity aspect is likely to furnish a useful method of approach.

In short, it is suggested that the concept, *sourness of soils*, is ambiguous, referring to two different conditions; one, an acid condition, and another, not understood, but probably associated with high reducing potentials. Without doubt the word "acidity" is often used where the broader term "sourness" would be better justified.

THE SIGNIFICANCE OF REDUCING CONDITIONS IN SOILS

It appears to be well accepted that good soils are normally oxidizing, and that reducing conditions are an indication of an unhealthful state of affairs. The term "oxidizing" has been used in a broad sense by previous writers; and differences in degree of oxidation have been in terms of quantity, not of intensity. Reducing conditions have as a rule been recognized, either by the absence of oxidation, or by the presence of specific substances of known reducing power. Ferrous carbonate, which can be present only under reducing conditions, has been taken as the toxic agent concerned in badly drained soils. This can hardly be the only specific toxic reducing body present. A correlation has been noted between the occurrence of aldehydes and soil infertility (32), and a characteristic property of aldehydes is their reducing power. It has been found (18) that, in cane fields, soil from poor spots often showed greater reducing power for ferric salts than soil from good spots, and reference was made to the well-known reducing function of bacteria and of organic substances.

Honing (16) contrasted his unfavorable results, obtained with the method of Gerretsen (12), with the interesting results obtained by the latter. Honing states (in a summary in English):

By this method Gerretsen could discern what soils were in good condition and what in a poor, not sufficiently oxydated one, as the soils with a high hydrogen-iodide value gave a rich crop of sugar or rice, and those with a low value, a small crop. . . . . When this method of testing irrigated soils on Java was tried on dry soils in Deli, it proved to be im-

practicable . . . . the very high hydrogen-iodide value of soil samples taken 30–90 cm. beneath the surface is caused not by a *higher degree of oxydation* of the soil at that distance from the free air, but by the *large quantity* of oxydated material, i.e., ferric iron. This ferric iron is not equally divided over the whole depth. . . . .

This seems to be a clear illustration of the failure of a method based on the quantity factor alone.

In the light of the reduction-potential measurements of the writer, bacterial cultures are apparently normally reducing, and soils may become highly reducing if water-logged for a few days in the laboratory. It is very possible that similar changes will occur under field conditions, certainly under conditions of very poor drainage, and possibly, during periods of wet weather, in fields where the drainage is comparatively good. It would seem worth while to adopt the working hypothesis that a given intensity of reduction, as expressed by the reduction potential, has an equal biological effect in the soil, irrespective of the chemical reactions involved in producing the potential.

There can be no doubt that something is lacking in present methods of approach to the problem of soil aeration. Cannon and Free (4) state that "Although deficiency in aeration has frequently been suggested as an agricultural difficulty, or as the reason why certain species do not grow upon soils of heavy texture, it does not appear that this suggestion has had any exact experimental basis, ..." They appear to think that the question may be handled by means of gas analysis, but, just as the hydrogen-electrode potential is able to distinguish degrees of acidity and alkalinity in regions beyond the limits in which we can detect concentrations analytically, so is the reduction potential capable of distinguishing differences in degree of reduction in regions where oxygen can no longer be detected at all by gas analysis. If a curve is drawn, such as has been given by Wells (39), showing the concentrations of oxygen and hydrogen which would be in equilibrium with an unattackable electrode at various reduction potentials (in the presence of a suitable catalyst), it becomes obvious that the region capable of study by gasometric methods is only a small part of the possible field. Cannon and Free, however, made interesting observations by means of gasometric analysis; as did also Russell and Appleyard (30), who detected significant variations in certain patches of a field under different weather conditions. It may be doubted whether variations could be detected in this way in water-logged soils after any considerable period of immersion. In the cultivation of rice and other irrigated crops it is a matter of great importance to know when to remove the excess water. In a popular article (1) the importance of the subject has been recently emphasized, and the suggestion been made that practical application might be feasible of any principles which may be found.

We may interpret the fact that the quality of a soil is correlated with the quantity of substance produced in a test for oxidative power as follows. The bodies responsible for the reactivity of the soil in these tests may be

supposed to be carriers of oxygen. The intensity factor of oxidation or reduction will not vary in great degree with changes in the concentration of these bodies, but they may protect the soil against reducing conditions for a limited time. When the soil is well aerated they are oxidized, and when the oxygen supply is too low they serve to supply oxygen to the soil constituents, so that a large supply of carriers is generally favorable.

Some soils become highly reducing when water-logged. The addition of organic substance aids in the production of reducing conditions, as reported above for peptone, and especially for dextrose. There can be no doubt that other organic substances have more or less action of this kind. Now, a considerable amount of work has been done upon the toxic effect of green manure in soils; this will not be reviewed here in detail. The subject has recently been discussed by Fred (10) in relation to the failure of seedlings. It is desired here to point out only that the toxic action of green manure is not well understood; it can in certain cases be attributed to infection of the plants with parasites (10), but naturally it is difficult to bring convincing proof as to whether the infection is the primary trouble, or a secondary one. It appears well worth consideration, whether the primary trouble may not be a high intensity of reduction.

SUMMARY

Oxidation and reduction potentials are discussed as the intensity factor of oxidation and reduction. Measurements of the reduction potentials of bacterial cultures or suspensions showed, when suitable precautions were taken, constant potentials for the facultative anaerobe B. coli, and for mixed cultures of soil microorganisms grown in a deep layer; the values for the reduction potentials being near the hydrogen electrode potentials. Measurements with aerobes (B. subtilis, B. mycoides, and a third aerobe), showed progressively increasing reduction potentials with lapse of time, but in no case did the reduction potential approach the hydrogen-electrode potential as closely as 0.3 volt. It is thought that this difference between anaerobes and aerobes may hold in general, but the evidence is not conclusive.

When soils were treated with an excess of water they became highly reducing, as evidenced by their reduction potentials. At the same time their hydrogen-electrode potentials changed. In the cases noted the changes of hydrogen-ion exponent indicated by the hydrogen-electrode potentials were very considerable, the soils becoming less intensely acid.[8] Accompanying the development of reducing conditions was a production in most cases of a foul odor.

[8] Because of the abnormal properties of the water-logged soils, which might lead one to suspect a poisoning of the electrode (even though no evidence of poisoning was seen), no emphasis will be placed on this result at this time. The result seemed to the writer to require confirmation by the colorimetric method. However, Mr. L. A. Hurst of this laboratory has recently seen the same result, using the colorimetric method, in the case of a sample of Caribou loam.

Different soils differed in the rate at which they became highly reducing. The addition of dextrose to one soil favored the development of reducing conditions, the effect of 0.1 per cent of dextrose being very pronounced.

It is thought that "sourness" of soils includes something beyond acidity, and that the residual unfavorable quality may be a high intensity of reduction. A discussion is given of the significance of reducing conditions and of reduction potentials in soil study.

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FURTHER STUDIES ON THE FREEZING-POINT LOWERING OF SOILS AND PLANTS

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In an earlier contribution (1) we presented results of our investigations on the effect of certain environmental conditions on the freezing-point lowerings of the cell sap of the roots and tops of several crops. It was shown that the density of the cell contents of the leaves of plants increases from early morning until noon and again decreases in the evening, being lowest at night. The loss on drying at 100°C. was greatest at sunrise and in the evening. The increase in concentration of the cell sap, however, continues after the loss on drying becomes constant. On the other hand, when the plants are shaded the density tends to decrease during the day and no increase in the loss on drying is noted. As a result of greenhouse and field studies it was concluded that the concentration of the cell sap of the roots of plants is markedly and rapidly affected by changes induced in the concentration of the soil solution by the addition of soluble salts as well as a decrease in the water content of the soil mass. As the water content of the soil decreased the density of the cell sap of the roots increased, the freezing-point lowerings approaching each other at the wilting point. On the other hand, the tops of plants were found to be less sensitive to the changes in the soil solution. Interesting data were obtained from crops grown on the same and different soils under field conditions. The dilatometer was employed in attempts to account for the daily fluctuations in the freezing-point lowerings of the cell sap of the leaves of plants. Less water was found to freeze in the barley tissue taken at noon than that sampled early in the morning.

It has been considered advisable to repeat some phases of these investigations and to continue others. Additional information has been obtained, some of which appears in this contribution.

WATER THAT FREEZES IN PLANT TISSUE UNDER DIFFERENT TEMPERATURES

The dilatometer has been employed in attempts to determine whether or not there is any relationship between the concentration of the soil solution, cell sap and the water that freezes in plant tissue at different temperatures. In making the determination, a sample of the fresh tissue is quickly weighed and inserted into the bowl of the dilatometer and ligroin added. Air bubbles are removed by stirring the tissue; the process may be hastened somewhat

217

by means of a vacuum or suction pump. In determining the amount of water that freezes readily 10 gm. of the tissue may be used and the determination made in a freezing mixture of −1.5°C. The dilatometer is allowed to remain without agitation until the mass reaches the temperature of the bath, precautions being taken to prevent solidification. When this temperature is attained the dilatometer is agitated somewhat and solidification takes place. When equilibrium is established the reading is taken. It was found advisable to use a smaller amount of the tissue when employing markedly colder baths, inasmuch as there is a tendency for freezing to occur before the entire mass has reached the temperature of the bath. With some plants 2 gm. is the most practicable amount while with others four or five may be used.

Rye, wheat, corn, sweet clover and red clover were employed. The results presented in table 1 show the freezing-point lowerings of the leaves of several crops and also the amount of water that froze at temperatures of −1.5°C.

TABLE 1

The amount of water freezing in leaves of plants at different temperatures

CROP	DATE	WEIGHT OF MATERIAL	FREEZING-POINT DEPRESSION	−1½°C.	−4°C.	COOLED TO −15°C. WARMED TO −4°C.	COOLED TO −15°C. REFROZEN AT −4°C.
		gm.	°C.	cc.	cc.	cc.	cc.
Rye................	November 24	5	0.928	0.90	2.50	2.55	2.70
Rye................	May 17	5	1.030	0.86	2.40		
Wheat.............	November 24	5	1.107	0.40	2.65	2.45	2.45
Sweet clover........	November 24	5	0.906	1.22	2.82	2.61	2.61
Clover.............	May 15	5	0.780	1.70	2.70		
Corn...............	June 10	5	0.578	2.10	2.90		

and −4°C. In addition determinations were made on rye and clover leaves at temperatures of −2°C., −4°C. and −6°C., respectively. The results go to show that there are wide differences in the water that freezes in the different crops at the higher temperature; the crops that we used having the lowest concentration of cell sap as determined by the freezing-point method gave up the largest amounts. The differences are less striking when the determinations are made at−4°C. or −6°C.

The amount of water that readily freezes in plant tissue should be of general interest to plant physiologists and it is probable that a knowledge of it would be valuable, especially where the changes in the concentration of the cell contents of plants as well as winter injury are being investigated.

The effect of low temperature also was determined. The dilatometer containing the tissue was placed in a bath the temperature of which was maintained at −15°C. until equilibrium was established, and then transferred to the −4°C. bath and the reading again taken when equilibrium was attained. Moreover, the tissue was frozen at −15°C., then thawed and refrozen at

−4°C. The low temperature increased somewhat the amount of water freezing in rye at −4°C., and decreased it somewhat in case of wheat and sweet clover. In preliminary experiments rye and clover leaves were subject to a temperature of −78°C. but the effect on the amount of water freezing at the higher temperature was slight. While more water undoubtedly froze at the lower temperature the concentration of the cell sap was such that thawing occurred when the material was warmed to −4°C.

EFFECT OF CONCENTRATION OF SOIL SOLUTION ON THE FREEZING-POINT LOWERINGS OF ROOTS AND TOPS OF PLANTS

The effect of the concentration of the soil solution on the freezing-point lowerings of the roots and leaves of plants at different periods was studied further. In addition the effect of this factor on the amount of water in the leaves freezing at −2.5°C. and −4.5°C. was investigated. The plants were grown in a house the roof and walls of which were made of oiled muslin. As shown in plate 2, the house was so constructed that the roof could be removed and the walls lowered, thus admitting direct sunlight and permitting a free circulation of air. With this arrangement it is believed that the conditions in so far as light and air are concerned are as nearly those of the field as can well be obtained.

A heavy sandy loam was used, the soil being packed into 3-gallon jars by hand so as to reduce variations to a minimum. Sufficient soil was added so that it could be rounded up above the sides of the jar. It was then covered with wax in order to prevent any rain which might by accident leak into the house, from entering the soil. Water was added through four $\frac{1}{2}$-inch glass tubes which extended about an inch below the surface of the soil and 5 or 6 inches above, and also through an inverted funnel which reached about half way to the bottom of the jar. Under the bowl of the funnel and extending somewhat beyond it was placed a perforated paraffined cardboard plate to act as a spreader for the water. By this means a fairly uniform water content could be maintained in the soil.

The following concentrations of the soil solution were decided upon as giving a sufficient range:

FREEZING-POINT DEPRESSION	MATERIAL IN SOLUTION	OSMOTIC PRESSURE
°C.	p.p.m.	atmospheres
0.160	4000	1.930
0.317	7920	3.821
0.490	12250	5.904

In order to bring the soil solution to the concentration desired $MgSO_4$, KH_2PO_4 and $Ca(NO_3)_2$ were used in the proportion recommended by Shive. These salts were dissolved in distilled water and the resulting solu-

tion used to moisten the soil. The strength of the solution necessary to use to afford the desired concentration in the soil was determined by mixing a small portion of the soil with enough solution to give a moisture content of 15 per cent and determining the freezing-point lowering by means of the Beckmann thermometer. The concentration of the solution of the soil also was determined as it was placed in the jars.

The jars were taken down at 8 a.m. and samples of the leaves obtained for determining the loss upon drying, the freezing-point lowerings, and also for

TABLE 2

The concentration of the cell sap of the roots and tops of barley grown in soils of different concentration and the per cent of water in the leaves which freezes. Period of growth 3 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Loss on drying at 100°C.	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	atmospheres	per cent	°C.	atmospheres	per cent		
0.100	1.209	15.53	0.909	10.948	87.74	52.92	70.56
0.284	3.423	13.88	0.949	11.428	88.12	55.10	73.87
0.499	6.012	14.47	0.995	11.980	87.63	54.01	69.61
0.112	1.350	15.70	0.847	10.210	88.05	57.32	73.87
0.255	3.074	15.33	0.832	10.527	88.38	57.32	73.86
0.379	4.567	15.81	0.905	10.90	87.95	55.10	72.77

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	atmospheres	°C.	atmospheres
0.400	4.821	0.330	3.978
0.610	7.349	0.430	5.182
0.775	9.334	0.570	6.867
0.365	4.399	0.285	3.435
0.580	6.988	0.395	4.760
0.650	7.830	0.490	5.904

the measurement of the amounts of water freezing at different temperatures. The soil was then emptied from the jars and the roots hastily removed. A portion of the roots was freed as far as possible from soil by shaking and the sample placed in a freezing tube which was stoppered and packed in ice. Another portion of the roots was washed free of soil with distilled water and dried between filter paper, care being taken not to crush the roots. They were then placed in a stoppered tube and packed in ice until the determinations could be made. The soil was thoroughly mixed and samples drawn for moisture and freezing-point determinations.

The data represent the average of duplicate determinations on the leaves of the plants and soil from each jar and where the amount of material on the roots permitted. The percentage of moisture in the tops and the amount of water freezing at different temperatures are calculated on the weight of fresh tissue.

The results obtained for barley after a 30-day period of growth are given in table 2. In the first set the plants in the jars with the lowest concentration of soil solution made the largest growth but were the worst infested with mildew. The plants grown in the soil of medium concentration were almost equal in height to the former while those grown in the soil of high concentration were much smaller.

In the second set the plants grown in the soil of medium concentration were more thrifty than those in the other jars. Where the soil had a low concentration the development was only slightly less, while in the jars of high concentration the plants were somewhat smaller and showed less root development.

The results in table 2 show a very slight tendency for the concentration of the cell sap of the tops of barley to increase as the concentration of the soil solution increases. The loss on drying at 100°C. and the percentage of water freezing as determined by means of the dilatometer likewise show little variation. More water froze at -4.5°C. than at -2.5°C., but there appears to be no relation between the amount of water freezing at either temperature and the concentration of the soil in which the plants were grown. On the other hand, the cell sap of the barley roots increased in concentration with each increase in concentration of the soil solution. This is true for both the washed and the unwashed roots.

On account of the infestation with mildew it was not deemed advisable to continue the growth of barley for a longer period, and in consequence corn was substituted.

The results for corn after a 30-day period compose table 3.

There was not a great deal of difference in the growth of the corn in the soil with medium and with high concentration, but where the concentration was low the production was about 50 per cent less. This is well shown by plate 3, figure 1.

According to the freezing-point lowerings of the soil the concentration of the soil solution was materially lowered and consequently the variations in concentration were not so great as desired. Notwithstanding this lack of great variation in the osmotic pressure of the soil solution at the end of the period of growth, in the first series there was a decided increase in concentration of the cell sap of the roots with each increase in concentration of the soil solution. In the second series there was an increase in concentration of the sap of the roots of the plants grown in the second jar over those produced in the first but those in the third showed no greater lowerings than those of the second. It appears, therefore, that while the concen-

tration of the soil solution at the time the experiment was completed did not vary as much as it did originally, the effects of the concentrations were still evidenced by the freezing-point lowering of the cell sap of the roots.

It is evident from the data obtained that the concentration of the cell sap of the tops of corn is not influenced so much by the concentration of the soil solution in which the plants are grown, as is the sap in the roots of the plants.

The variations in the moisture content of the tops were small. The per cent of water in the tops that froze at −2.5°C. did not change materially

TABLE 3

The concentration of cell sap of the roots and tops of corn grown in soils of different concentrations and the per cent of water in the tops which freezes. Period of growth 30 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Moisture content	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	atmospheres	per cent	°C.	atmospheres	per cent		
0.085	1.0237	15.81	0.569	6.861	85.52	50.71	66.12
0.120	1.392	16.01	0.550	6.628	84.62	51.80	63.94
0.120	1.447	16.28	0.672	8.101	83.83	42.98	69.44
0.075	0.904	16.15	0.523	6.296	85.14	52.92	61.73
0.182	2.200	15.13	0.575	6.927	84.97	55.1	63.89
0.295	3.556	15.87	0.577	6.952	84.45	45.20	70.56

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	atmospheres	°C.	atmospheres
0.245	2.953	0.250	3.014
0.387	4.670	0.313	3.779
0.577	6.957	0.390	4.700
0.422	5.091	0.275	3.315
0.590	7.108	0.380	4.580
0.577	6.957	0.375	4.519

except in the case of the plants grown in the third jar, in which it was appreciably less. The amount of water that froze at −4.5°C. was greater than at −2.5°C., the plants grown in the third jar of each series giving up more than the others. Apparently there is no correlation between the concentration of the cell sap of the leaves and the per cent of water that freezes. This view is supported by the results reported in table 1.

As previously pointed out, the concentration of the soil solution in the various jars has been so reduced that the desired differences did not exist. It seemed advisable, therefore, to add sufficient quantities of the salt solution

to maintain the original concentration. This was accomplished by frequently adding small quantities of the solution.

At the expiration of 60 days the corn in all cases had set ears. The silks were still fresh. The stalks in the jars of the lowest concentration were slender and the leaves of poor color. The plants growing in the soil of medium concentration were tall and sturdy and of good color. Where the high concentration was used, the stalks were larger in diameter than in the case of the jars of medium concentration, but much shorter. There was no apparent

TABLE 4

The concentration of the sap of the roots and tops of corn grown in soils of different concentrations and the per cent of water freezing. Period of growth 60 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Moisture content	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	atmospheres	per cent	°C.	atmospheres	per cent		
0.145	1.748	13.60	0.720	8.672	78.24	41.88	56.5
0.485	5.844	10.39	0.807	9.724	79.75	52.92	59.52
1.015	12.220	10.41	0.884	10.648	77.66	42.99	57.32
0.170	2.050	13.84	0.692	8.341	78.97	37.48	54.5
0.510	6.145	10.48	0.797	9.604	79.36	41.88	59.52
0.947	11.41	10.71	0.897	10.810	78.41	41.88	58.42

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	atmospheres	°C.	atmospheres
0.560	6.747	0.225	2.712
1.080	13.00	0.562	6.777
1.157	13.93	0.842	10.147
0.540	6.507	0.362	4.369
1.115	13.42	0.595	7.168
1.062	12.79	0.627	7.559

difference in the stage of maturity of the plants in the various jars. The variations in growth are shown by plate 3, figure 2.

The results of the freezing-point, dilatometer and moisture determinations on the plants and soil for the 60-day period are given in table 4.

There was a decided increase in osmotic pressure of the cell sap of the tops with the increase in concentration of the soil solution, this being more apparent than in the previous series, or the one of shorter duration. The losses entailed on drying the tops at 100°C. show little variation. Moreover, the water freezing at −2.5°C., except in the case of the plants grown in the

second jar, did not vary a great deal. When a bath of −4.5°C. was employed a larger amount of water was frozen, as was noted in the 30-day series. The amount was somewhat less in the plants grown in the soils of the lowest concentration than in the others.

In case of the unwashed roots the freezing-point lowerings of the plants from the second and third jars were greater than those grown in the first.

In the second and third jars of each series the concentrations of the root sap of the unwashed roots appeared to be greater than that of the corresponding tops, an unusual condition.

The washed roots show a steady increase in concentration with each increase of osmotic pressure of the soil solution.

In order to make sure that the increase in concentration was not due to an accumulation of soluble material on the surface of the leaves rather than to material actually in solution in the cell sap, some of the leaves were washed with distilled water and sampled several hours later. The results obtained from the washed and unwashed leaves are set forth in table 5.

TABLE 5

Effect of washing on the concentration of the cell sap of corn leaves

SOIL		UNWASHED LEAVES		WASHED LEAVES	
Freezing-point depression	Osmotic pressure	Freezing-point depression	Osmotic-pressure	Freezing-point depression	Osmotic pressure
°C.	atmospheres	°C.	atmospheres	°C.	atmospheres
0.145	1.748	0.720	8.672	0.645	7.770
0.485	5.844	0.807	9.724	0.710	8.552
1.015	12.220	0.884	10.648	0.712	8.576

These data show that when washed the correlation between the osmotic pressure of the cell sap of corn tops and that of the soil in which the plants were grown largely disappears. These results substantiate the conclusions of the writers in a previous paper (1), that the tops of plants are less sensitive to changes in concentration of the soil solution than are the roots.

THE EFFECT OF MOISTURE CONTENT OF SOILS ON THE CONCENTRATION
OF THE CELL SAP IN ROOTS AND TOPS OF PLANTS

Under field conditions plants are subjected to extreme and quite rapid variations in the moisture content of the soil. To what extent the water content of the soils affects the osmotic pressure of the cell sap of the roots and tops of plants, as well as the loss on drying and the per cent of water freezing in the tops at different temperatures, is of interest. To obtain additional information on these points barley was grown in 3-gallon jars of sandy loam containing various amounts of moisture. The data obtained are presented in table 6.

No differences were found in the concentration of the cell sap or in the loss on drying of the tops of plants grown in soils of different moisture content. However, the roots, both washed and unwashed, possessed a higher concentration of cell sap when grown in the soil of lower water content. The per

TABLE 6

The concentration of the cell sap of roots and tops of barley grown in soils of different moisture content and the per cent of water in the leaves which freezes. Period of growth 30 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Moisture content	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	*atmospheres*	*per cent*	*°C.*	*atmospheres*	*per cent*		
0.012	0.141	23.29	0.903	10.880	88.36	57.87	81.21
0.100	1.205	15.53	0.090	10.948	87.79	52.92	70.56

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	*atmospheres*	*°C.*	*atmospheres*
0.335	4.038	0.205	2.472
0.400	4.821	0.330	3.978

TABLE 7

Concentration of the cell sap of the roots and tops of corn grown in soils of different moisture content and the per cent of water in the leaves which freezes. Period of growth 60 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Moisture content	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	*atmospheres*	*per cent*	*°C.*	*atmospheres*	*per cent*		
0.412	4.965	0.712	8.576	8.237	44.10	44.10	63.94
0.162	7.469	0.592	7.132	8.376	51.80	51.80	84.88

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	*atmospheres*	*°C.*	*atmospheres*
0.614	7.406	0.419	5.055
0.357	4.301	0.279	3.369

cent of water that froze in the tops was less in those plants grown in the soil with lower water content, both when a −2.5°C. and a −4.5°C. bath was used; that is to say, the water content of the soil mass in which the plant grew affected the form in which the water existed in the plant tissue.

The results obtained for corn after 60 days' growth are to be found in table 7.

These data substantiate in general the conclusions drawn from the results obtained from the previous series. The increase in the amount of water that froze in the tops at $-2.5°C.$ with an increase in water content of the soil was not so regular as in the earlier series. The amount of water freezing at $-4°C.$, however, varied with the moisture content of the soil. In considering these data it must be remembered that while the concentration of the soil solution in the soil of each jar was quite low, yet that in the soil containing approximately 15 per cent of moisture was about ten times as dense as that of the soil containing 23 per cent. It must be admitted, therefore, that it is not clear from this series whether the differences in concentration of the cell sap of the roots is due to the differences in water content of the soil or the variation in concentration of the soil solution.

In order to determine the effect of different water contents of the soil on the concentration of the roots and tops of the plants growing in it, the concentration of the soil solution remaining the same, the next series of experiments was conducted. Jars of sandy loam were made up to 10, 15 and $22\frac{1}{2}$ per cent moisture content and sufficient salts (Shive's 3-salt nutrient solution) added to the soil containing 15 and $22\frac{1}{2}$ per cent water to give it practically the same concentration as that containing 10 per cent moisture.

The concentrations in the various jars at planting were:

	Freezing-point depression °C.
10 per cent H_2O jars	0.238
15 per cent H_2O jars	0.250
$22\frac{1}{2}$ per cent H_2O jars	0.260

The results for corn after a period of 30 days' growth are shown in table 8.

Notwithstanding the addition of salts the soil with high moisture content had less depression at the conclusion of the experiment than the soil of low water content. On the other hand, the concentration of the soil solutions in the soils of medium and of low water content approached sufficiently near to each other to allow of some conclusions being drawn from the results.

There is very little relation between the moisture content of the soil and the concentration of the cell sap of the tops and the moisture content of the tops of the plants grown in soil of low and of medium water contents. The per cent of water in the tops that froze at $-2.5°C.$ increased as the water content of the soil decreased. When a bath of $-4.5°C.$ was used, however, there was very little difference in the percentage of water that froze. These results are unlike those obtained from previous series in which the water content of the soil remained constant and the concentration of the soil solution varied, or the one in which the moisture content of the soil varied, no effort being made to control the concentration of the soil solution. This is quite interesting, as it raises the question of the influence of soluble salts in the soil solution on the free water in plant tissue with soils of varying moisture contents.

TABLE 8

Concentration of the cell sap of roots and tops of corn grown in soils of different moisture content the concentration of soil solution remaining constant. Period of growth 30 days

SOIL			TOPS				
Depression of freezing point	Osmotic pressure	Moisture content	Depression of freezing point	Osmotic pressure	Moisture content	Per cent of water freezing at	
						− 2.5°C.	− 4.5°C.
°C.	atmospheres	per cent	°C.	atmospheres	per cent		
0.097	1.145	23.50	0.625	7.529	85.66	41.88	59.52
0.310	3.736	15.31	0.642	7.740	86.58	46.30	63.94
0.242	2.923	10.77	0.622	7.499	84.87	52.92	63.94
0.137	1.603	21.00	0.632	7.619	85.75	41.88	63.94
0.232	2.802	15.34	0.650	7.830	86.01	44.10	61.74
0.275	3.315	9.86	0.605	7.289	85.18	52.92	61.18

UNWASHED ROOTS		WASHED ROOTS	
Depression of freezing point	Osmotic pressure	Depression of freezing point	Osmotic pressure
°C.	atmospheres	°C.	atmospheres
0.410	4.941	0.320	
0.525	6.326	0.415	5.001
0.672	8.101	0.370	4.459
0.440	5.302	0.365	4.399
0.525	6.326	0.425	5.122
0.665	8.010	0.460	5.543

SUMMARY

The amount of water that froze readily, or at −1.5°C. and at lower temperatures in the leaves of several crops, was determined. Wide variations in the amount of water that easily froze in the plants studied were found, the greatest taking place in those having low freezing-point depressions. The differences were much less striking when lower temperatures were employed. Larger amounts of water were found to freeze when lower temperatures were employed. However, subjection to very low temperature (−15°C.) resulted in the freezing of no more water at −4°C. when subsequent determinations were made at that temperature.

Considering all the data presented, the conclusion seems justified that the concentration of the cell sap of the roots of the plants used in these investigations is influenced quite decidedly by the concentration of the soil solution in which the plants are grown. While it is probable that determinations made on either the washed or unwashed roots do not represent the true concentration of the cell sap and while there are some variations in the results obtained,

yet considering the data as a whole, the above conclusion is warranted. The effect of the concentration of the soil solution was not so marked on the concentration of the cell sap of the leaves.

These results substantiate the conclusions drawn from work previously published.

Marked increases in the concentration of the soil solution induced by the addition of full nutrient solution of varying strength, the water content of the soil remaining constant, did not measurably alter the amount of water that froze at $-2.5°C.$ and $-4°C.$, respectively. If higher temperatures had been employed the results might have been somewhat different.

Corn and barley plants grown in a soil of high, of medium and of low water content possessed more easily freezable water when grown in the soil of higher water content. When the water content varied and the concentration of the soil solution was maintained practically constant by the addition of a nutrient solution, more water froze at $-2.5°C.$ in the leaves of the plants grown in the soils of low water content. There was very little difference in the amount of water that froze at $-4°C.$ These results are quite interesting and somewhat at variance with the results obtained when both the water content of the soil and the concentration of the soil solution varied.

It is desired to call attention to the possibility of utilizing the dilatometer method for investigations in plant physiology.

REFERENCE

(1) McCOOL, M. M., AND MILLAR, C. E. 1917 The water content of the soil and the composition and concentration of the soil solution as indicated by the freezing-point lowerings of the roots and tops of plant. *In* Soil Sci., v. 3, no. 2, p. 113.

PLATE 1

FIG. 1. Plant house closed. Front view.
FIG. 2. Plant house closed. Rear view.

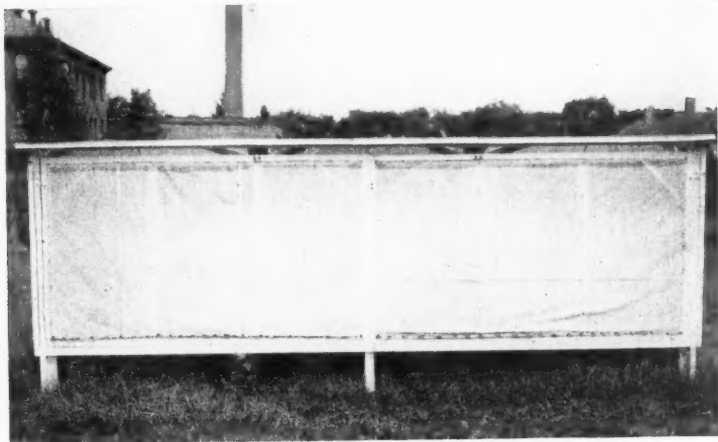FIG. 1
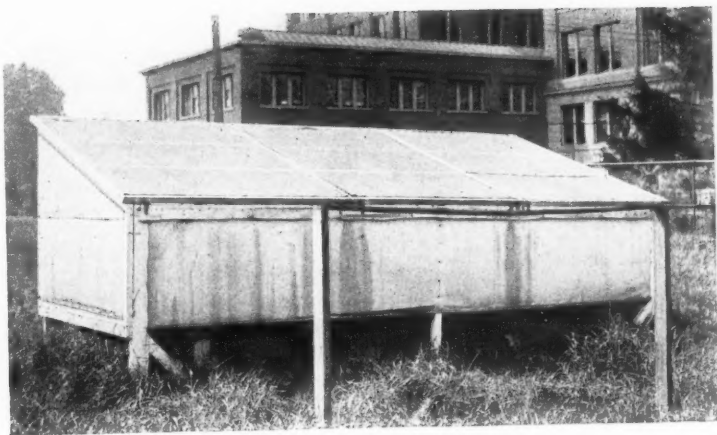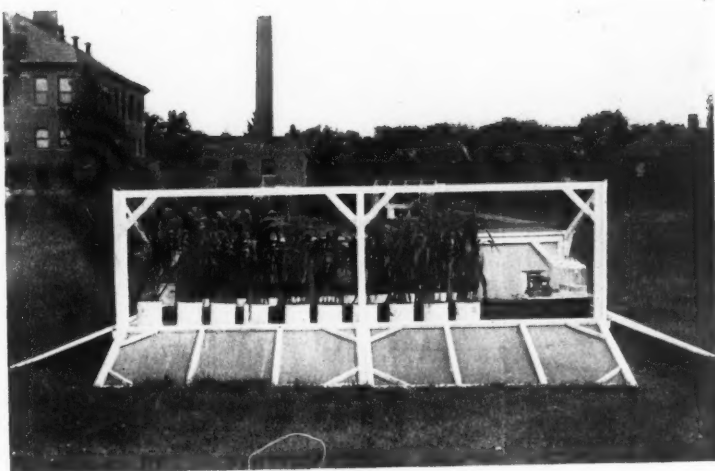

FIG. 2

PLATE 2

PLATE 3

FIG. 1.   Corn.   Period of growth 30 days.   Osmotic pressure of soil solution at time of planting: No. 1, 1.93 atmospheres; No. 2, 3.821 atmospheres; No. 3, 5.904 atmospheres.

FIG. 2.   Corn.   Period of growth 60 days.   Osmotic pressure of soil solution: No. 1, 1.748 atmospheres; No. 2, 5.844 atmospheres; No. 3, 12.220 atmospheres.
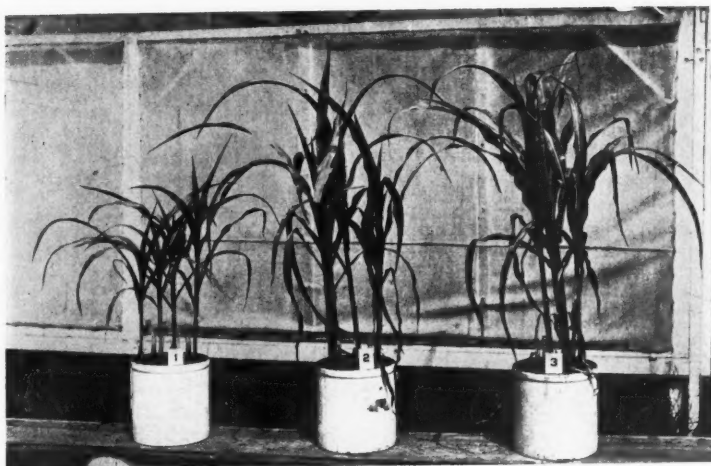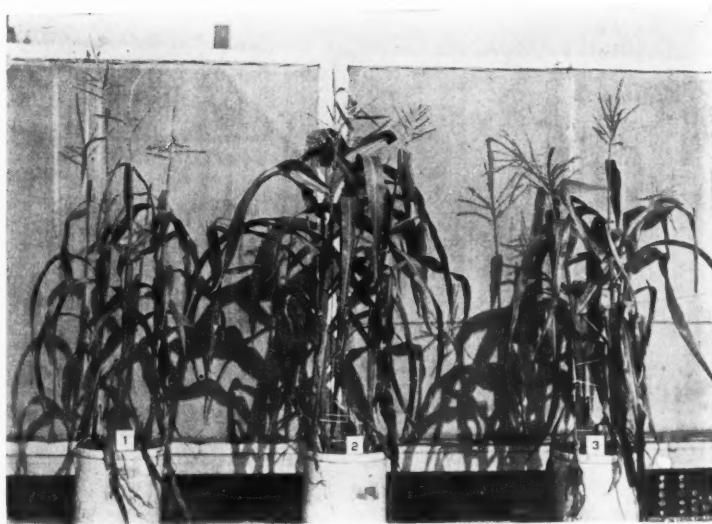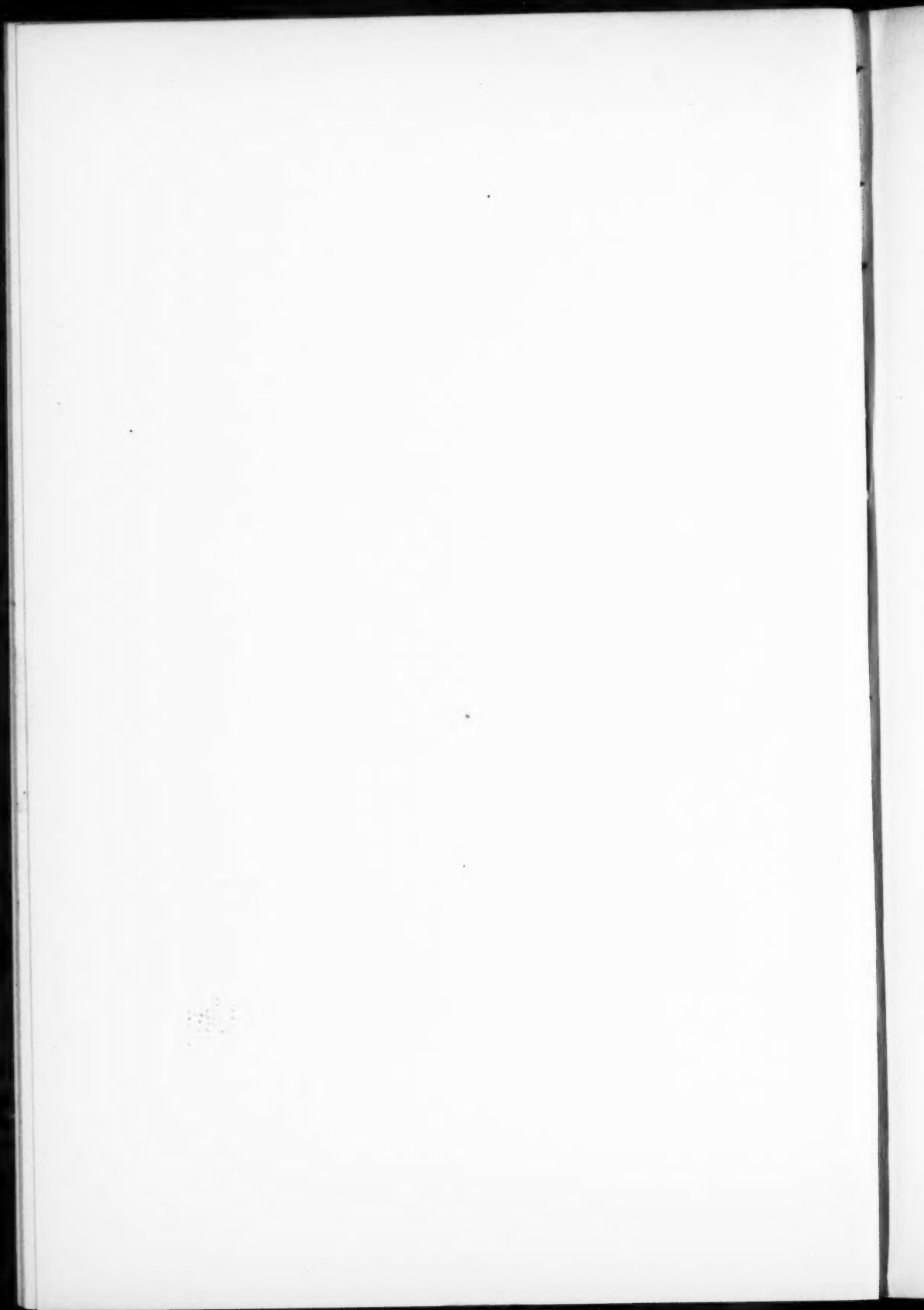
Fig. 1

Fig. 2

THE EFFECT OF LEACHING ON THE AVAILABILITY OF ROCK PHOSPHATE TO CORN[1]

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Insoluble plant-food materials become available to the plant only through the influence of some active agent. The carbonic acid in the soil produced by the growing plant and by biological processes, is no doubt the most important agent. The action of carbonic acid on insoluble plant-food materials, such as rock phosphate, follows the laws of mass action and chemical equilibrium, and may be represented as follows:

$$Ca_3(PO_4)_2 + 2H_2CO_3 \rightleftarrows Ca_2H_2(PO_4)_2 + CaH_2(CO_3)_2$$

Any changes of the masses or concentrations of the compounds of this system will cause a change in the equilibrium. If a plant removes both of the soluble products formed, in the proportion produced, the reaction will proceed indefinitely. If, however, the plant removes the soluble phosphate and only a lesser proportion of the calcium bicarbonate, a point of equilibrium will be established in which there will be proportionately more of the soluble calcium bicarbonate present. The continued removal of the soluble phosphate and only a partial removal of the calcium bicarbonate will finally result in such a large accumulation of the calcium bicarbonate and a consequent change in the equilibrium that the concentration of soluble phosphate will become insufficient for plant growth. On the basis of these considerations, Truog (9) has developed his theory in regard to the feeding power of plants for insoluble phosphates, which is stated as follows:

Plants containing a relatively high calcium oxide content have a relatively high feeding power for the phosphorus of rock phosphate. For plants containing a relatively low calcium oxide content, the converse of the above is true. The explanation of this relation is made possible by means of the laws of mass action and chemical equilibrium.

Chirikov (3) also believes that there is a direct correlation between the calcium needs of the plant and its ability to use insoluble phosphates.

In view of this theory, it appears that if in some manner the soluble calcium bicarbonate could be entirely or in part removed by leaching, or even moved about in the soil medium or made more soluble through the use of certain salts, equilibrium would at least not be established so quickly and it would be possible for a relatively weak feeding plant to utilize insoluble phosphates to a greater degree. An acid condition of the soil which gives a certain capacity to combine with basic materials and hence remove calcium bicarbonate from solution, has been shown by Prianichnikov (6) Kossowitch (4) and others to increase the availability of insoluble calcium phosphates to many plants.

EXPERIMENTAL

Plan of work

The investigations reported herein were planned primarily to test the effect of leaching on the availability of rock phosphate. As a test crop, corn was selected because it nicely fulfills the requirements of being a poor feeder on insoluble phosphates, uses only a little calcium, and is a comparatively rapid grower.

The plants were grown in a greenhouse in 2-gallon, glazed earthenware pots. Each pot was provided with a $\frac{5}{8}$-inch hole on the side just above the bottom for drainage. In the unleached pots these holes were partly closed with a cork stopper in which a small groove had been cut to facilitate air movement, and to carry away any excess water that might be present. To facilitate drainage in the leached pots these holes were provided with rubber stoppers, through which passed a slightly bent glass tube, protected on the inside by a small bunch of glass wool. To each pot was added 11,000 gm. of pure white quartz sand with which the phosphate treatments indicated in table 1 had been thoroughly mixed.

Five seeds of a standard variety of corn were planted in each pot and later thinned to the best three plants. All treatments were duplicated.

The nutrient solution used was made up from single-salt stock solutions which were prepared by dissolving separately in liter portions of water, 68 gm. of sodium nitrate, 32 gm. of ammonium nitrate, 20 gm. of potassium sulfate, 8 gm. of magnesium sulfate, and 0.4 gm. of ferric chloride. The standard application of these solutions was 10 cc. of the first four, and 1 cc. of the last, diluted as desired, usually to 1 liter. The two solutions of nitrogen salts indicated, carried the same amount of nitrogen. Only one form of nitrogen salt was used on a single culture, as indicated in table 1. After growth was well started, applications were made once each week. Both the phosphorus and calcium had to be secured by the plant from the calcium phosphates mixed in the sand. Calcium nitrate was applied to the check pot.

The moisture content of the unleached pots was maintained by frequent weighings, at about 13 per cent of the weight of the sand. No attempt was made to maintain a definite moisture content in the leached pots, as the plants were grown under well drained conditions with sufficient moisture.

Each week the one set of pots was leached with the nutrient solution until approximately 1 liter of drainage water was secured from each pot. Later these leachings were made twice a week. The solutions from the leachings were filtered immediately through Pasteur-Chamberland clay filters, and the filtrates retained for determinations of the calcium content.

The plants were harvested just as the tassels were beginning to appear. One set of duplicates was used after securing the green weights for determinations of the plant sap acidity which is to be reported in another paper (1). A sample from each pot was retained for dry-matter determinations. The other set was harvested, and all the material was weighed and dried for dry-matter content and chemical analysis. The general appearance at harvest time is shown in plate 1.

Effect of treatments on plant growth

The data of weights indicating growth are summarized in table 1, and are graphically shown in figure 1.

Leaching the soil had a decided influence upon the availability of the rock phosphate to the corn plant. This was true where either form of nitrogen salt accompanied the rock phosphate. The smallest yield was secured from the unleached pot (no. 39) treated with $NaNO_3$. With this treatment the soil solution probably became saturated with calcium bicarbonate, which greatly hindered the further solution of the phosphate, as explained by the laws of mass action and chemical equilibrium. Evidently the nutrient solution containing the $NaNO_3$ had little or no solvent effect on the rock phosphate. The data for the leached pot (no. 47) show a striking increase in yield. Under these conditions the soil solution was freed from the excessive amounts of calcium bicarbonate, and in accordance with the laws of mass action and chemical equilibrium, more phosphate was brought into solution. This increase in growth is more clearly brought out in plate 2 which shows these plants after the sand had been washed out of the roots.

Analogous results were secured when NH_4NO_3 was used with rock phosphate instead of $NaNO_3$. The yields, however, were much higher for both the leached and the unleached pots. The increase due to leaching under these conditions was very much greater than when $NaNO_3$ was used. These differences could have been due only to the influence of NH_4NO_3. Evidently this salt increased the solubility of the calcium bicarbonate more than $NaNO_3$; it thus changed the point of equilibrium and caused the reaction making the rock phosphate available to proceed with greater rapidity. The NH_4NO_3, as is indicated further on, probably also acted as a physiologically acid salt. The use of NH_4NO_3 thus allowed greater growth in both the leached and the unleached pots than $NaNO_3$. The greatest growth of all was produced with a combination of rock phosphate, NH_4NO_3 and leaching (pot 51).
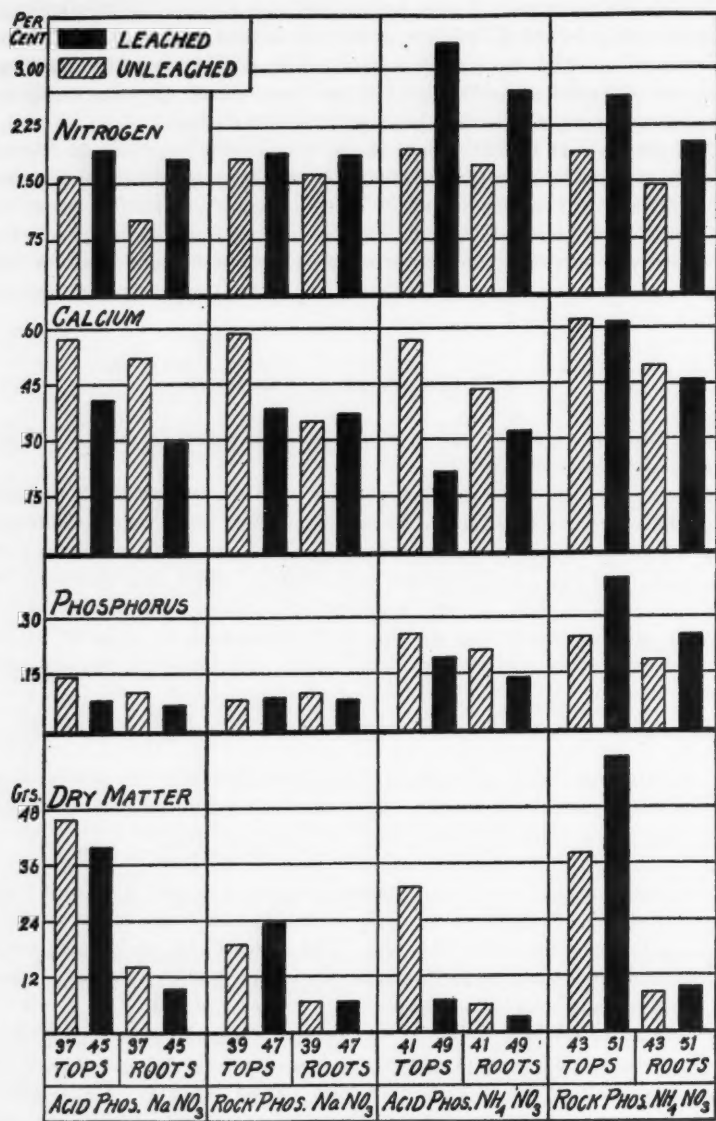
FIG. 1. EFFECT OF LEACHING ON THE WEIGHT OF DRY MATTER, AND CONTENT OF
PHOSPHORUS, CALCIUM AND NITROGEN OF CORN GROWN WITH THE TREATMENTS
INDICATED

Leaching the pots treated with acid phosphate gave poorer results than no leaching.   In fact, the results due to leaching with acid phosphate are just the opposite to those secured with rock phosphate.   With $NaNO_3$ leaching definitely decreased the yield but not excessively.   With NH_4NO_3, however, leaching very decidedly decreased the yield, and the poorest yield of all cultures, outside the check pot, was produced in the leached pot (no. 49) where acid phosphate was used with NH_4NO_3.   Here it appears, as will be shown

TABLE 1

The green and dry weights, water content, and comparative dry weights of corn produced with treatments indicated

POT NO.	TREATMENT*	AVERAGE WEIGHTS OF DUPLICATES				COMPARATIVE DRY WEIGHT† OF TOPS	WATER AS PER CENT OF GREEN WEIGHT	
		Green		Dry				
		Tops	Roots	Tops	Roots		Tops	Roots
		gm.	gm.	gm.	gm.		per cent	per cent
35	Check....................................	7.0	18.1	1.9	1.2	4.2	73.6	93.1
37	Acid phosphate, NaNO₃, unleached............	236.9	146.2	45.2	13.3	100.0	80.9	90.0
45	Acid phosphate, NaNO₃, leached..............	225.2	113.0	39.0	8.4	86.3	82.7	92.6
39	Rock phosphate, NaNO₃, unleached	72.0	82.6	18.3	6.2	40.5	74.6	92.4
47	Rock phosphate, NaNO₃, leached.............	126.9	99.9	23.4	6.9	51.7	81.5	93.1
41	Acid phosphate, NH₄NO₃, unleached..........	209.6	92.6	31.2	6.0	69.0	85.1	93.6
49	Acid phosphate, NH₄NO₃, leached.............	68.8	53.8	7.0	3.0	15.4	89.7	94.5
43	Rock phosphate, NH₄NO₃, unleached..........	194.4	74.0	38.8	8.2	85.8	80.0	88.9
51	Rock phosphate, NH₄NO₃, leached............	308.3	133.3	58.9	10.5	130.3	80.9	92.1

* Phosphate applications on the acre basis were 400 pounds of acid phosphate and 2000 pounds of rock phosphate.

† Growth with treatment of acid phosphate, NaNO₃ and no leaching, is represented by 100.

in the paper on the hydrogen-ion concentration of the plant juices and the soil solution (1), that leaching increased the acidity sufficiently to make conditions unfavorable for plant growth.

The effect of leaching where acid phosphate was used was evidently not a question of removing soluble calcium bicarbonate, as is the case where rock phosphate was used, but was one of changing the environment in other ways, which here appeared to have rather marked injurious effects.   These injurious conditions probably resulted from a lack of sufficient basic material.

Effect of treatments on plant composition

Leaching the soil also increased the water content of the plants. This was probably due to the decrease in the concentration of salts in the soil which favored greater availability of water to the roots. The percentage of water in the roots was greater than in the tops.

Table 2 gives the content of phosphorus, calcium and nitrogen as determined by analysis of the tops and roots of the plants grown with the different treatments. These results along with the dry weights are shown graphically in figure 1, where comparisons of the effect of the various treatments may easily be made.

TABLE 2

The content of phosphorus, calcium, and nitrogen in corn plants grown with the treatments indicated. Data are averages of duplicates

POT NO.	TREATMENT*	PHOSPHORUS		CALCIUM		NITROGEN	
		Tops	Roots	Tops	Roots	Tops	Roots
		per cent	per cent	per cent	per cent	per cent	per cent
35	Check...............................	0.074	0.063	0.835		2.11	0.60
37	Acid phosphate, NaNO₃, unleached............	0.135	0.102	0.571	0.522	1.59	1.02
45	Acid phosphate, NaNO₃, leached.............	0.086	0.075	0.407	0.297	1.95	1.84
39	Rock phosphate, NaNO₃, unleached...........	0.083	0.101	0.558	0.355	1.85	1.61
47	Rock phosphate, NaNO₃, leached.............	0.088	0.084	0.386	0.370	1.92	1.85
41	Acid phosphate, NH₄NO₃, unleached..........	0.258	0.212	0.553	0.433	1.96	1.73
49	Acid phosphate, NH₄NO₃, leached	0.195	0.132	0.219	0.313	3.38	2.74
43	Rock phosphate, NH₄NO₃, unleached..........	0.248	0.187	0.616	0.501	1.90	1.43
51	Rock phosphate, NH₄NO₃, leached............	0.402	0.248	0.611	0.459	2.66	2.07

* Phosphate applications on the acre basis were 400 pounds of acid phosphate and 2000 pounds of rock phosphate.

Just as there was a wide variation in the amounts of dry matter produced, there was also a wide variation in the contents of phosphorus, calcium and nitrogen. The degree and direction of the variation, however, were not the same for the three elements.

Leaching the soil increased the phosphorus content of the corn plant when rock phosphate was used, and decreased it when acid phosphate was used. The highest content of phosphorus occurred with NH₄NO₃. With NaNO₃ the phosphorus content was rather uniform. In general, the percentage content of phosphorus varied in the same direction as growth, but with smaller fluctuations.

The calcium content of the corn plants was in most cases greatly decreased by leaching. The increased growth due to leaching, when rock phosphate

was used, was accompanied by a higher phosphorus content, and in general, a lower calcium content. This is to be expected when the availability of rock phosphate is considered in connection with the laws of mass action and chemical equilibrium.

The calcium content of the tops from all unleached pots was quite uniform. When $NaNO_3$ was used the calcium content of the tops from leached pots shows but slight variation, but when NH_4NO_3 was used the results are quite divergent. The use of acid phosphate and NH_4NO_3 with leaching (pot 49) gave the lowest calcium content of tops of all cultures, and the use of rock phosphate, under similar conditions (pot 51), gave the highest calcium content.

The nitrogen content of the corn plant was increased by leaching. This increase was expecially marked when NH_4NO_3 was used. With no leaching the nitrogen content of all plants was quite uniform. Just why leaching should have caused the plant to take up more nitrogen, with no definite relation to growth, is not clear. With the NH_4NO_3 it may be that the NH_4 ion partly functioned as a base in place of the calcium. With acid phosphate the calcium content was very low, and this seems much more probable than with rock phosphate, in which case the plant appears to have had all the calcium it needed. This explanation is in harmony with the calcium content of the corn plant as noted above.

Effect of treatments on the calcium content of the drainage waters

Table 3 presents the data showing the soluble calcium derived from the rock phosphate and removed by leaching. Figure 2 graphically shows the influence of NH_4NO_3 as compared to $NaNO_3$ on the formation of soluble calcium, and hence availability of rock phosphate. It will be noted that the first leaching in both cases gave a rather large amount of soluble calcium. This, no doubt, represents the calcium of the rock phosphate that is readily soluble, and explains why there is but little difference with the two salts in the first leaching. After the first leaching the influence of the NH_4NO_3 on the solubility of the calcium becomes more and more marked.

The influence of $NaNO_3$ and NH_4NO_3 on the availability of rock phosphate

The results in table 3 are in harmony with the theory of the availability of rock phosphate in relation to the laws of mass action and chemical equilibrium. Sodium nitrate has little or no influence on the reaction, while NH_4NO_3 gives rise to conditions which increase the solubility of the calcium and change the point of equilibrium to a marked extent. This increases the solubility of the phosphorus in the rock phosphate and allows greater plant growth. When these larger amounts of calcium bicarbonate and other soluble calcium salts are removed by leaching, the availability of the rock phosphate and consequently plant growth, is further greatly accelerated. It will be noted that
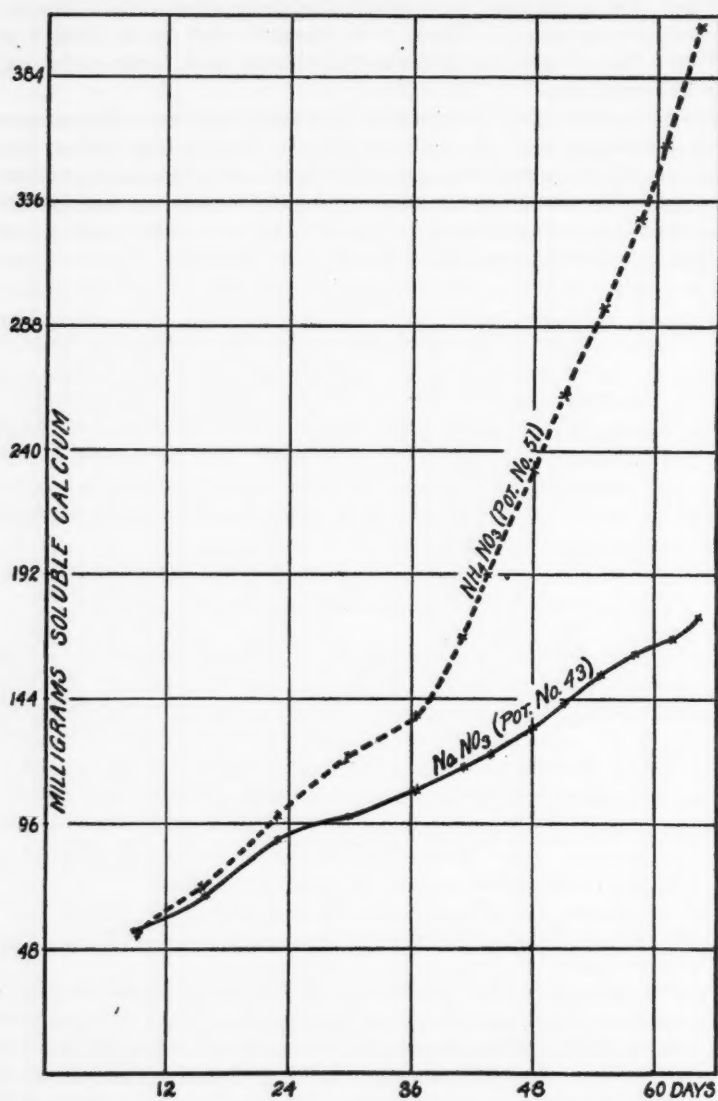
FIG. 2. INFLUENCE OF NH₄NO₃ COMPARED WITH NaNO₃ ON THE LEACHING OF
CALCIUM BICARBONATE FROM ROCK PHOSPHATE IN CORN CULTURES

practically three times (actually 2.9) as much calcium was leached from the pot (no. 51) containing NH_4NO_3 as out of the similar pot (no. 47) containing $NaNO_3$. The growth in the former was 2.5 times as great, which is in rather close agreement with the removal of calcium.

The influence of NH_4NO_3 on the availability of rock phosphate has been observed by Kossowitch (5), Prianichnikov (7) and Shulov (8), who explain it as due entirely to the action of NH_4NO_3 as a physiologically acid salt. Burlison (2), on the other hand, who used NH_4NO_3 in his nutrient solution, states that the solution had no appreciable influence on the availability of the rock phosphate in his experiments.

TABLE 3

The amounts of soluble calcium derived from rock phosphate and removed by leaching

NUMBER OF DAYS FROM BEGINNING OF EXPERIMENT	TOTAL CALCIUM REMOVED FROM EACH POT		RATIO OF SOLUBLE CALCIUM REMOVED BY NaNO₃ AND NH₄NO₃
	NaNO₃	NH₄NO₃	
	mgm.	*mgm.*	
9	53.88	53.37	1.0
16	13.63	18.75	1.3
23	21.63	27.02	1.2
30	10.38	23.69	2.3
37	8.25	15.14	1.8
41	9.37	30.10	3.2
44	7.45	27.32	3.6
48	7.11	36.19	5.0
51	10.81	31.72	3.0
55	11.09	33.02	3.0
58	5.70	31.21	5.4
62	8.09	30.50	3.8
65	9.09	46.18	5.0
Total..............	176.48	404.21	2.3
Total without first....	122.60	350.84	2.9

There is no question, however, from the results reported herein, but that the NH_4NO_3 did have a marked influence on the availability of the rock phosphate.

As has been briefly indicated, the favorable influence of the NH_4NO_3 on the availability of the rock phosphate may have been due to its effect on the solubility of the calcium bicarbonate, or to the increased acidity resulting from nitrification or more rapid removal of the NH_4-ion than of the NO_3-ion by the growing plant, or to all these factors combined. The sharp upward bend in the curve for the NH_4NO_3 after about 36 days of plant growth, shown in figure 2, indicates that the production of soluble calcium was not alone dependent upon the direct chemical action of NH_4NO_3. Evidently the biological factors acting on NH_4NO_3 became more important at this point. This is

substantiated by the determinations of the hydrogen-ion concentrations or acidity which will be reported in a later paper (1). In all cases the soil medium and plant juices were more acid when NH_4NO_3 was used.

In order to determine more fully the comparative direct chemical effect of the nutrient solutions containing either NH_4NO_3 or $NaNO_3$ on the solubility of calcium bicarbonate and availability of rock phosphate, a battery of six percolators was arranged, in which distilled water and the complete nutrient solutions, containing either $NaNO_3$ or NH_4NO_3, were allowed to act with and without carbon dioxide on rock phosphate for 48 hours at room temperature. Each percolator contained 600 cc. of either distilled water or nutrient solution

TABLE 4

Soluble phosphorus and calcium in successive extractions of rock phosphate with the solutions indicated

TREATMENTS	FIRST EXTRACTION		SECOND EXTRACTION		THIRD EXTRACTION		TOTAL FOR THREE EXTRACTIONS	
	Phosphorus	Calcium	Phosphorus	Calcium	Phosphorus	Calcium	Phosphorus	Calcium.
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
H₂O	1.92	9.62	0.8	6.41	1.28	8.02	4.00	24.05
Nutrient solution with NaNO₃	2.16	17.64	0.56	8.82	1.76	13.13	4.48	39.59
Nutrient solution with NH₄NO₃	1.56	19.25	1.00	10.43	1.68	11.63	4.24	41.31
H₂O with CO₂	5.84	28.07	5.00	17.64	4.80	19.25	15.64	64.96
Nutrient solution with NaNO₃ and CO₂	7.04	34.49	5.28	22.45	5.88	22.86	18.20	79.80
Nutrient solution with NH₄NO₃ and CO₂	7.76	42.50	5.48	23.26	5.70	24.46	18.94	90.22

TABLE 5

The comparative solubility effects on rock phosphate of nutrient salts containing nitrogen as $NaNO_3$ and NH_4NO_3 calculated from data in table 4

NUTRIENT SALTS	WITHOUT CO₂		WITH CO₂	
	Phosphorus	Calcium	Phosphorus	Calcium
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
Salts containing NaNO₃	0.48	5.54	2.56	14.84
Salts containing NH₄NO₃	0.24	7.26	3.30	25.26

and 4.6 gm. of rock phosphate, which is the same proportion in which these materials were used in the pot cultures. Effective agitation was maintained in the one case by the bubbling of CO_2 from a tank, and in the other by the aspiration of CO_2-free air. The results obtained are given in table 4. A direct comparison of the solubility effects on rock phosphate of either $NaNO_3$ or NH_4NO_3 in conjunction with other nutrient salts may be made by subtracting the amounts of soluble phosphorus and calcium produced with the distilled or carbonated water from the amounts of these soluble materials produced when the nutrient salts were added to these. Figures from such subtractions are given in table 5.

The nutrient solution containing either $NaNO_3$ or NH_4NO_3 increased the availability of the rock phosphate to some extent over that of water. Without CO_2 there was but little difference in the effect of the two salts. With the addition of CO_2, which makes the conditions more closely comparable to those in pot cultures, the NH_4NO_3 was more effective than the $NaNO_3$, especially in the production of soluble calcium. From the data presented it appears that the influence of NH_4NO_3 upon the availability of rock phosphate is only in part due to its effect on the solubility of the calcium bicarbonate. Its capacity to produce an acid medium, as has been found, by acting either as a physiologically acid salt or by becoming nitrified, is probably an important factor in this connection.

GENERAL DISCUSSION

The data presented herein show that leaching the soil increases the availability of rock phosphate to corn. This fact is manifested by increased growth and a higher percentage content of phosphorus in the plant. Accompanying the increase in growth, there is found a proportionate increase of calcium in the solutions from the leachings and a lower percentage content in the plant. These results are readily explained by the laws of mass action and chemical equilibrium, and are in harmony with Truog's theory (9) concerning the utilization of insoluble phosphates by crops.

Carbonic acid is no doubt the principal agent in these reactions. The soluble calcium in the leachings and the results obtained indicate this. The main source of carbonic acid in quartz cultures of this kind is that which is excreted by the growing plant through its roots. As it is formed and comes in contact with the rock phosphate both soluble phosphorus and soluble calcium bicarbonate are produced. These compounds are in equilibrium with the insoluble phosphate and the carbonic acid. The corn plant has greater need proportionally for the soluble phosphate than it has for the soluble calcium; hence the soluble phosphorus is assimilated and much of the calcium is left behind. As the calcium bicarbonate accumulates in the soil it tends to bring about equilibrium and thus suppress the formation of soluble phosphorus. When this condition exists, the plant has access to large amounts of available calcium but little phosphorus, and consequently the plant shows a high calcium and low phosphorus content and a stunted growth. When the soil is leached the excess of soluble calcium bicarbonate is removed from the root zone and thus the point of equilibrium in the reaction with rock phosphate is not so rapidly attained, and more phosphorus becomes available to the plant. Greater growth results and the plant shows a higher phosphorus and a lower calcium content. Plants that have a relatively large need for calcium would therefore be better feeders on rock phosphate than those that have but little need for calcium, as pointed out by Truog.

The data show further that accompanying fertilizers may directly increase the solubility of the calcium bicarbonate or even produce an acid medium and thus increase the availability of the rock phosphate by delaying the rapidity with which the equilibrium is established. Ammonium nitrate as compared with sodium nitrate shows marked influences in these respects. Nearly three times as much soluble calcium was found in the leachings from the NH_4NO_3-treated pots as in those from the $NaNO_3$-treated pots. This indicates that there should be a proportionate increase in the soluble phosphorus formed and consequently greater growth. The results show that growth increased in about the same ratio.

SUMMARY

1. Leaching the soil increased the availability of rock phosphate to corn by removing the excess of soluble calcium bicarbonate and other soluble calcium salts. These results are in accord with the laws of mass action and chemical equilibrium.

2. Ammonium nitrate had a marked influence on the solubility of rock phosphate to corn, due to its favorable effect on the solubility of calcium bicarbonate, and its capacity to produce an acid medium either by acting as a physiologically acid salt or by becoming nitrified.

3. Sodium nitrate had no appreciable influence on the availability of rock phosphate.

4. The soluble calcium leached from the pots treated with rock phosphate under the influence of $NaNO_3$ and NH_4NO_3 was found to be in the ratio of 1:2.9. The growth ratio of corn under the same conditions was 1:.2.5, showing therefore, a rather definite relation between the calcium leached out in solution and plant growth.

5. Leaching caused a decrease in the production of dry matter where acid phosphate was used.

6. Ammonium nitrate with acid phosphate appeared to cause a physiological disturbance in the plants, especially with leaching. This was probably due to the insufficiency of basic material.

7. The phosphorus content of the corn plants increased with increased growth.

8. Leaching decreased the calcium and increased the nitrogen content of the plants.

9. Leaching increased the water content of the plants, as a result, undoubtedly of the lessened concentration of soluble salts in the soil medium.

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PLATE I

THE EFFECT OF LEACHING AND OF THE FORM OF PHOSPHATE AND NITROGEN SALT ON THE
GROWTH OF CORN

Pot no.	Treatment
35	Check
37	Acid phosphate, $NaNO_3$, unleached
45	Acid phosphate, $NaNO_3$, leached
39	Rock phosphate, $NaNO_3$, unleached
47	Rock phosphate, $NaNO_3$, leached
41	Acid phosphate, NH_4NO_3, unleached
49	Acid phosphate, NH_4NO_3, leached
43	Rock phosphate, NH_4NO_3, unleached
51	Rock phosphate, NH_4NO_3, leached

PLATE 1

EFFECT OF LEACHING ON ROCK PHOSPHATE
F. C. BAUER
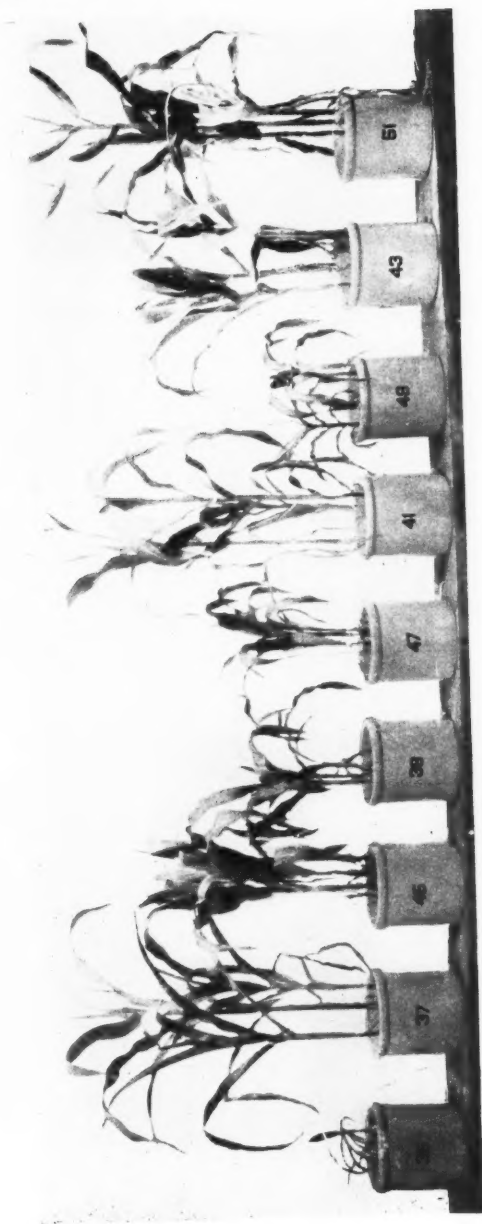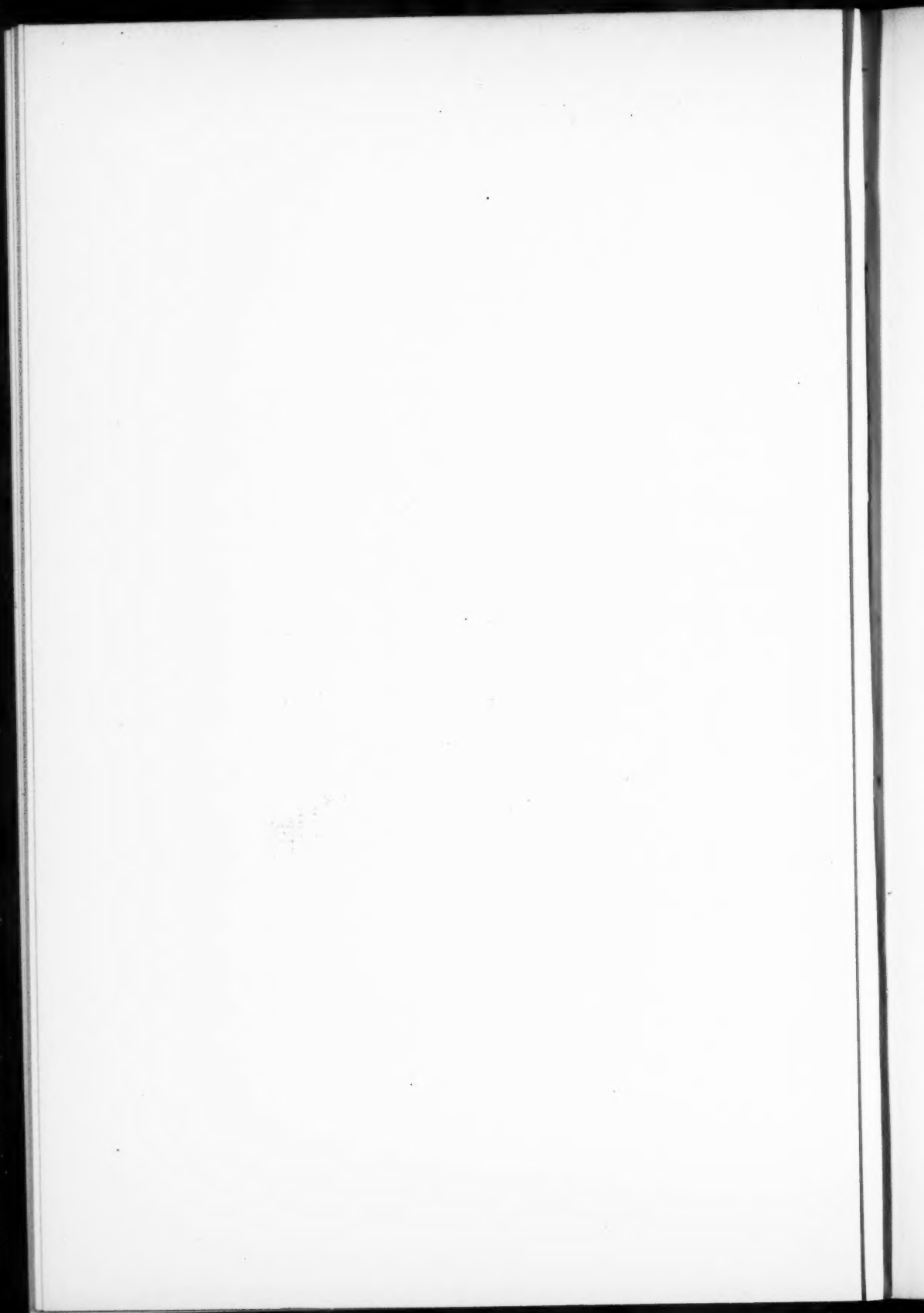
PLATE 2

THE EFFECT OF LEACHING ON THE AVAILABILITY OF ROCK PHOSPHATE TO CORN

Pot no.	Treatment
1	Leached (pot 45)
2	Unleached (pot 39)

F. C. BAUER

THE LIME REQUIREMENT OF SOILS ACCORDING TO THE VEITCH METHOD, COMPARED WITH THE HYDROGEN-ION CONCENTRATION OF THE SOIL EXTRACT

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The measurement of the hydrogen-ion concentration of solutions has recently come into quite general favor. When the proper apparatus has been set up or color standards prepared, it is a rapid method and gives very satisfactory results.

Thus far, the method has not been widely used by soil investigators. Gillespie (2) has reported electrometric and colorimetric results on 22 samples of soil from different parts of the country. Gillespie and Hurst (3, 4) have used this method to determine the reaction of potato soils in relation to the presence or absence of the scab fungus and it is quite possible that it may have a wide application in this connection.

Martin (8) has used it for the same purpose and also for determining the relative hydrogen-ion concentration of extracts from soils to which varying amounts of sulfur were applied.

It is not quite clear to what extent the method may be employed in the determination of the lime requirement of soils. In this connection, Gillespie and Hurst say:

> It will be recalled that the intensity of acidity is measured by the hydrogen-ion concentration, and that it bears in general no simple or direct relation to the quantity of acid present. It has been shown many times that the hydrogen-ion concentration possesses a greater significance in biochemical processes than the quantity or concentration of acid substance. It is therefore entirely possible that certain problems of soil fertility, especially those relating to the necessity or desirability of liming for any specific crop, which have not as yet been solved by means of determinations of "lime requirement," may be solved by measurements of hydrogen-ion concentration.

Sharp and Hoagland (11, 12) have made determinations of hydrogen-ion concentrations of suspensions of unground soil, of soil ground to pass a 200-mesh screen and of heated soil. They also used the electrometric titration method in an attempt to determine the lime requirement by adding to the soil suspension, standard calcium hydroxide until a definite alkaline solution was obtained. This work they supplemented by pot and beaker studies.

Kappen and Zapfe (6) determined the titratable acidity and the hydrogen-ion concentration in extracts of peat soils and of peat and humus-forming plants.

Hoagland and Sharp (5) have studied the hydrogen-ion concentration of soil suspensions under various partial pressures of carbon dioxide.

Plummer (9) used the hydrogen electrode in determining the reaction of a large number of untreated soils in suspension. He also determined the reaction of soils that had received different fertilizing materials.

Rice and Osugi (10) heated soil with a solution of cane sugar, determined the quantity of invert sugar, and in another portion of the filtrate determined the hydrogen-ion concentration by the color method of Sörensen.

In some recent work in connection with the lime experiments which are being conducted at this station, the authors had an opportunity to compare lime requirement data secured by the Veitch method with the hydrogen-ion concentration of water extracts from the same soils. We do not maintain that results obtained by the one method may be directly interpreted in terms of the other, but feel that the data secured are of sufficient importance to warrant publication. The soils in question were taken from plots which are laid out in four different 5-year rotation systems, with seven plots for each system. For a full description of these plots and the lime treatment see Lipman and Blair (7). The lime treatment for each rotation system is as follows:

Plot 1..check (no lime)
Plot 2...½ ton calcium limestone per acre
Plot 3...1 ton calcium limestone per acre
Plot 4..2 tons calcium limestone per acre
Plot 5...½ ton magnesian limestone per acre
Plot 6...1 ton magnesian limestone per acre
Plot 7..2 tons magnesian limestone per acre

The soil is a Sassafras loam inclining to the gravelly phase. Previous to 1908, the land had been neglected for a number of years. Limestone was applied in accordance with the above plan, first in the spring of 1908 and again in the spring of 1913 and of 1918.

The four rotations as carried out during the period of 1913 to 1917 were as follows:

	ROTATION 1, PLOTS 21-27	ROTATION 2, PLOTS 28-34	ROTATION 3, PLOTS 35-41	ROTATION 4 PLOTS 42-48
1913	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)
1914	Oats (soybeans and cowpeas)	Potatoes	Potatoes (rye)	Oats and peas, millet
1915	Wheat	Rye	Tomatoes (rye, vetch, crimson clover)	Rye and vetch, rape
1916	Timothy and clover	Timothy and clover	Lima beans (rye, vetch, crimson clover)	Rye, cowpeas (rye)
1917	Timothy and clover	Timothy and clover	Cucumbers (rye and vetch)	Oats and peas, cowpeas

For the period of 1908 to 1912 the crops were practically the same as for 1913 to 1917.

TABLE 1

Lime requirement and hydrogen-ion concentration of soils from plots that have received different quantities of lime

PLOT NUMBER	SPECIAL TREATMENT	LIME (CaO) REQUIRE-MENT PER 2,000,000 POUNDS OF SOIL		pH VALUES, 1919
		1913	1919	
	Rotation 1: General farm crops			
		lbs.	*lbs.*	
21	Nothing....................................	1,200	1,500	5.4
22	0.5 ton CaCO₃ per acre..........................	1,000	500	6.1
23	1.0 ton CaCO₃ per acre..........................	600	400	6.7
24	2.0 tons CaCO₃ per acre.........................	000	000	7.2
25	0.5 ton CaCO₃MgCO₃ per acre....................	600	400	6.0
26	1.0 ton CaCO₃MgCO₃ per acre....................	700	100	6.5
27	2.0 tons CaCO₃MgCO₃ per acre..................	000	000	7.0
	Rotation 2: General farm crops			
28	Nothing....................................	800	1,200	5.8
29	0.5 ton CaCO₃ per acre.........................	800	400	6.0
30	1.0 ton CaCO₃ per acre..........................	600	000	6.5
31	2.0 tons CaCO₃ per acre.........................	100	000	7.1
32	0.5 ton CaCO₃MgCO₃ per acre....................	700	800	6.3
33	1.0 ton CaCO₃MgCO₃ per acre....................	400	000	6.7
34	2.0 tons CaCO₃MgCO₃ per acre..................	300	000	6.9
	Rotation 3: Corn, potatoes, market garden crops			
35	Nothing....................................	1,100	1,600	5.5
36	0.5 ton CaCO₃ per acre..........................	800	1,200	6.1
37	1.0 ton CaCO₃ per acre..........................	600	200	6.3
38	2.0 tons CaCO₃ per acre.........................	400	000	7.1
39	0.5 ton CaCO₃MgCO₃ per acre....................	1,100	800	6.2
40	1.0 ton CaCO₃MgCO₃ per acre....................	700	600	6.5
41	2.0 tons CaCO₃MgCO₃ per acre..................	500	000	6.9
	Rotation 4: Forage crops			
42	Nothing....................................	1,200	800	5.4
43	0.5 ton CaCO₃ per acre..........................	1,100	600	6.0
44	1.0 ton CaCO₃ per acre..........................	700	400	6.3
45	2.0 tons CaCO₃ per acre.........................	600	000	7.1
46	0.5 ton CaCO₃MgCO₃ per acre....................	1,100	400	6.2
47	1.0 ton CaCO₃MgCO₃ per acre....................	500	200	6.4
48	2.0 tons CaCO₃MgCO₃ per acre..................	300	000	6.9

The samples of soil were collected during the fall of 1919 so that something over a year had elapsed since the last application of limestone. In collecting the samples, nine borings were made at different points in the

$\frac{1}{15}$-acre plot and these were then thoroughly mixed; brought to the laboratory where they were dried and passed through a 1-mm. sieve preparatory to analysis. Lime-requirement determinations were made by the Veitch method and at the same time, the hydrogen-ion concentration of the soil extract was
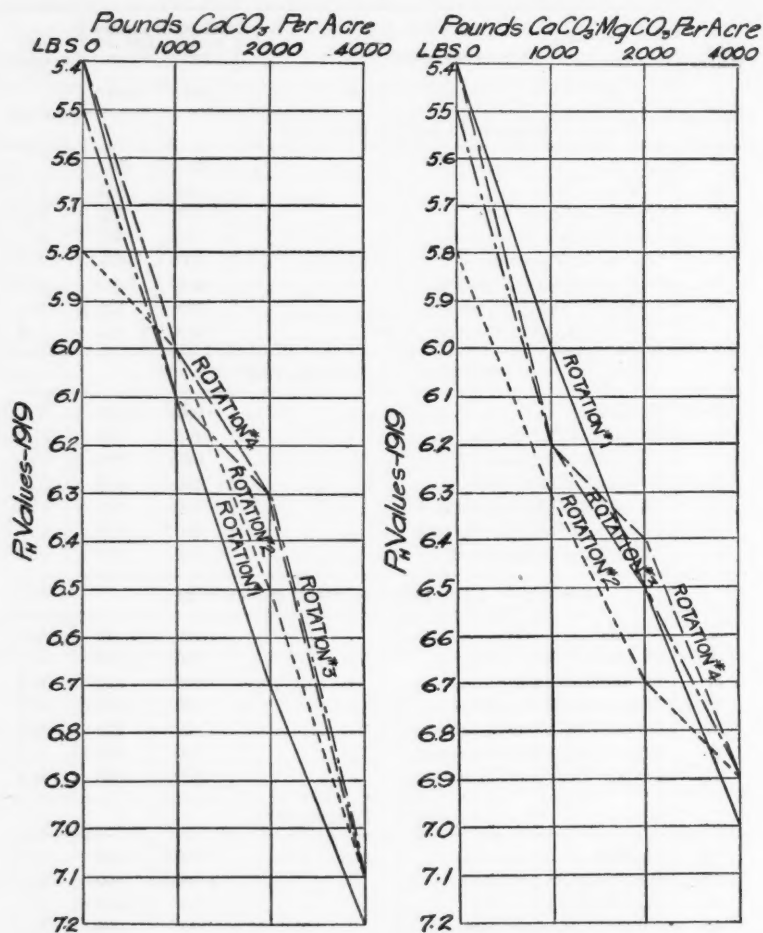

FIG. 1. DIAGRAM OF pH VALUES

determined by using the phenolsulfonphthalein series of indicators suggested by Clark and Lubs (1). The soil extract was prepared by shaking 15 gm. of soil with 30 cc. of distilled water and centrifuging until a clear solution was obtained. The results from the two methods are shown in table 1. From this it will be noted that almost without exception the lime requirement

·decreased as the amount of limestone applied was increased.   However, the decreases are not necessarily proportional to the amount of limestone applied.

With an application of 1000 pounds of CaCO₃ the range in lime requirement for rotations 1, 2 and 4 is from 600 to 400 pounds per acre, and the hydrogen-ion exponent expressed as pH, using the terminology of Sörensen, is about 6.1. The corresponding sample from rotation 3 shows a requirement of 1200 pounds, and a pH value of 6.1.   It will be noted that the pH value in these two cases is practically the same, and in this connection it is well to remember that the
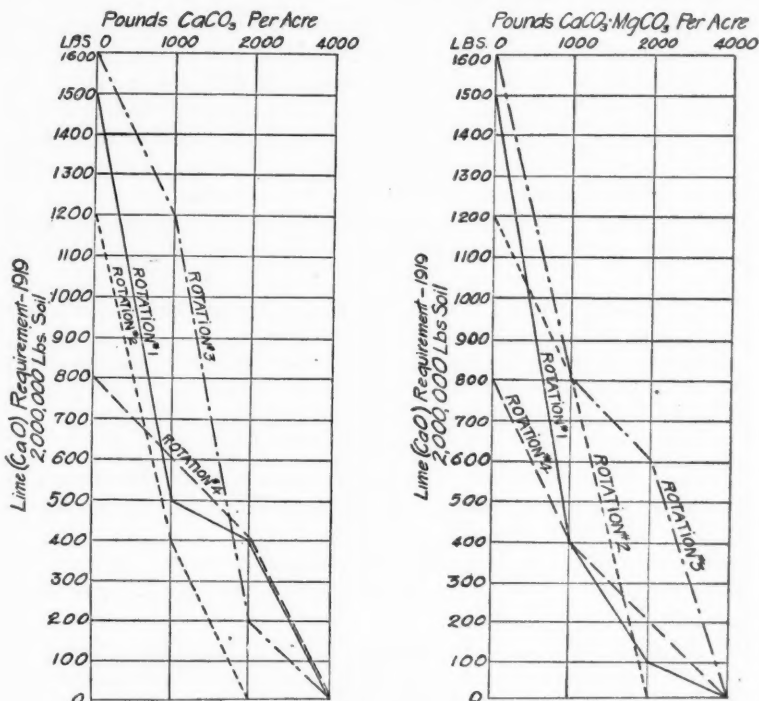

FIG. 2.   DIAGRAM OF LIME REQUIREMENTS ACCORDING TO THE VEITCH METHOD

hydrogen-ion concentration is a measure of the intensity of acidity and not of the titratable acidity.   With 1000 pounds of the magnesian limestone, the lime requirement varies from 800 to 400 pounds per acre and the hydrogen-ion exponent from 6.0 to 6.3.   With 2000 pounds of the limestone, both calcium and magnesium, the lime requirement varies from 600 pounds to an alkaline reaction, and the hydrogen-ion exponent from 6.3 to 6.7.

With the 4000-pound application of limestone, the Veitch method gives the alkaline reaction in all cases (this method, of course, can not show any distinction in degree of alkalinity), and the hydrogen-ion exponent varies

from 7.1 to 7.2 with the calcium limestone and from 6.9 to 7.0 with the magnesian limestone.

The pH values over 6.7 require no lime.

Between pH = 6.3 and 6.7,   800 pounds is the maximum requirement.

Between pH = 6.0 and 6.3, 1200 pounds is the maximum requirement.

Between pH = 5.4 and 6.0, 1600 pounds is the maximum requirement.

Although the lime requirement may fall much below the maximum given here, it would be a distinct advantage to know the maximum requirement at a certain hydrogen-ion concentration.

Further work must be done on a variety of soil types before any general conclusions can be drawn.   Tests have shown that soils containing high percentages of organic matter, such as muck soils, do not show any direct relationship between the hydrogen-ion concentration of the soil extract, and the lime requirement by the Veitch method.   In such cases the lime requirement is much higher than would be expected from the pH values.   This is no doubt due to "buffer" materials which are present in such soils.

· For the check plots where no lime was added the lime requirement varies in the four rotations from 1600 to 800 pounds and the pH values from 5.4 to 5.8.

The differences referred to are more clearly brought out in the accompanying graphs.

A study of the pH values shown in table 1 leads to the following suggestions.

SUGGESTIONS

1. For the samples tested, there appears to be a fairly close correlation between the hydrogen-ion concentration of the soil extract and the lime requirement as determined by the Veitch method.

2. Certain inconsistencies appear which may be due to the inaccuracies of the Veitch method or to the lack of uniformity in the samples, or to the influence of "buffer" substances.

3. With normal soils, a determination of the hydrogen-ion concentration of the soil solution may give one some idea of the amount of lime water required by the Veitch method, and thus considerably shorten this method.

4. Of the soils under consideration, those which have a hydrogen-ion concentration of about pH = 6.7 or over, are alkaline by the Veitch method.

5. With further studies along this line, it may be possible, with normal soils, to assign a fairly definite lime requirement to a given hydrogen-ion concentration, so that in many cases at least a determination of the hydrogen-ion concentration would make a lime-requiremernt determination unnecessary. If such should prove to be the case, the gain in time will be an important item.

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HYDROGEN-ION CONCENTRATION MEASUREMENTS OF SOILS IN CONNECTION WITH THEIR "LIME-REQUIREMENTS"

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The work on hydrogen-ion concentration measurements of the soils is still in its infancy. Notwithstanding the importance of such measurements in soil-fertility problems very little has been done in this field. In biochemical work hydrogen-ion concentration measurements are of enormous significance as pointed out by Michaelis (4) and Clark and Lubs (1). Sharp and Hoagland (5) report on the acidity and absorption in soils as measured by the hydrogen electrode. Gillespie and Hurst (3) call attention to the fact that it is possible to exploit hydrogen-ion concentration studies in problems of soil fertility, especially those connected with "lime-requirements" in general, and specific crops in particular. The soil may be looked upon in a way, as a culture medium for microorganisms which have a direct bearing upon soil fertility. Reaction studies of the soil are being conducted at the New Jersey station, and this paper is simply a report on some work bearing indirectly on the subject.

The question of how much lime should be applied to a particular field for a certain crop has not as yet been answered satisfactorily in the light of studies of the intensity of the acidity, as measured by the hydrogen-ion concentration method. We must, for the present, use the old Veitch method and its numerous modifications, with all their deficiencies. The determination of the lime-requirement by the Veitch method requires a preliminary investigation on the approximate acidity of a given soil; this is followed by the trial method of determining the titrable acidity. In this method and many of its modifications the reaction best suited to the particular crop is not taken into consideration, and in this respect they are of no value.

An attempt was made to see whether there is a correlation between the lime requirement as determined by the Veitch method and the curve of pH values resulting from the lime-water treatment.

Table 1 gives a description of the soils used in the work.

The hydrogen-ion concentration of these soils, as expressed in pH values, was determined by the colorimetric method, using the phenolsulfonephthalein indicator series as described by Clark and Lubs (1). The results appear in Table 2.

Those soils that approached the neutrality point were treated with little lime-water; this did not, however, give any idea as to how much lime-water

261

TABLE 1

Description of soils used

LABORA- TORY NUMBER	TYPE OF SOIL	TREATMENT	REMARKS
1	Mud bottom; mostly vegetable residues		Good cranberry-producing soil
2	Savannah bottom; mostly sand; little organic matter		Good cranberry-producing soil
3	Iron-ore bottom; mostly vegetable residues		Good cranberry-producing soil
4	Mud bottom; sandy soil with much organic matter	4000 pounds of limestone per acre applied in 1914.	First half-inch surface soil
5	Same as 4, but less organic matter		Second half-inch surface soil
6	Still less organic matter		From first to second inch depth
7	Mostly sand		From second to fourth inch depth

Soil 8, 9, 10, 11, is a check on 4, 5, 6, 7; no lime applied

12	Mud bottom; much organic matter, resembles soil 8	Concentrated sulfuric acid applied to kill weeds	No cranberries grown
13	Savannah bottom; mostly sand	4000 pounds of limestone per acre applied in 1918	
14	Mud bottom; sandy soil with much organic matter		
15	Iron-ore bottom; very little organic matter		
16	Mud bottom; same as 14		Check on soil 14
17	Mostly sand; some undecayed vegetable matter	Sulfuric acid applied to kill weeds, followed by limestone to correct acidity	No cranberries
18	Same as 17	Acid applied, but no lime	No cranberries

TABLE 1—*Concluded*

LABORA-TORY NUMBER	TYPE OF SOIL	TREATMENT	REMARKS
19	Mostly sand, but considerable vegetable matter	Sulfuric acid applied first, then rock phosphate	No cranberries
20	Same as 19	Acid applied but no rock phosphate	No cranberries
21	Mostly vegetable residues	No treatment	First half-inch of surface soil
22	Same as 21 but a little sand in addition	No treatment	Second half inch of soil
23	Same as 22 with still more sand; but mostly vegetable residue	No treatment	From first to second inch depth
24	Same as 23 with somewhat more sand	No treatment	From second to fourth inch depth

TABLE 2

Hydrogen-ion concentration of soils compared with lime requirement according to the Veitch method

LABORATORY NUMBER	pH VALUE BEFORE TREATMENT	LIME-WATER REQUIRED FOR NEUTRALIZATION AS DETERMINED BY THE VEITCH METHOD (1 CC. OF LIME WATER=0.009607 GM. CaO).	pH VALUE BEFORE EVAPORATING SAMPLE FOR THE LIME REQUIREMENT DETERMINATION BY THE VEITCH METHOD	pH VALUE AFTER EVAPORATION
		cc.		
1	5.2	50.00	6.9	8.2
2	4.8	25.00	7.2	8.0
3	5.2	49.00	7.0	8.0
4	7.0	1.00	6.8	7.9
5	6.4	5.00	6.8	8.0
6	6.2	10.00	6.6	8.0
7	5.8	10.00	6.8	8.1
8	5.0	48.00	7.0	7.9
9	5.4	26.00	6.9	7.9
10	5.0	40.00	7.0	8.1
11	5.4	15.00	7.1	8.2
12	5.0	52.00	6.8	8.0
13	5.4	22.00	7.0	8.2
14	6.0	30.00		8.0
15	6.2	8.00	6.7	8.2
16	4.4	40.00	6.6	8.0
17	4.6	45.00	7.1	8.2
18	4.2	60.00	6.8	8.0
19	4.4	45.00	7.0	8.2
20	4.2	65.00	6.6	8.0
21	4.0	78.00	6.8	8.0
22	4.0	65.00	6.9	8.2
23	4.1	60.00	6.9	8.2
24	3.9	50.00	6.9	8.2

was to be used. The procedure, therefore, consisted of the regular Veitch method. With every trial, on a fresh addition of lime, the pH values were determined before and after evaporation. In the case of the sandy soil samples, which are rather poor in organic matter, less lime-water was required to reach the maximum (the point where the solution turns pink after evaporating the filtrate, in the Veitch procedure) independently by the initial pH value than with those that had a higher humus content. This can easily be seen in table 2. Samples 1 and 3, soils consisting chiefly of organic material, required 49 and 50 cc. of lime-water, although the original pH value was 5.2 in each case, while sample 2, which was of a sandy nature, required only 25 cc. with an original pH value of 4.8, i.e., a more acid reaction than either samples 1 or 3. The same is noticeable in the case of the other samples.
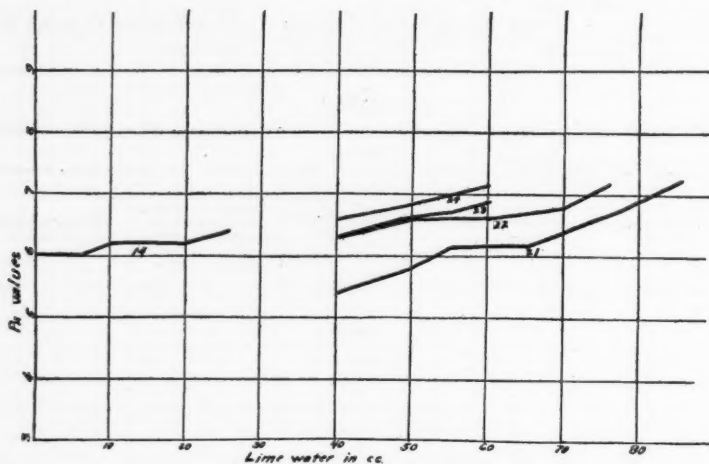

FIG. 1. CURVES OF HYDROGEN-ION CONCENTRATION OF SAMPLES 14, 21, 22, 23 AND 24

The explanation for this is apparent. The sandy soil has no buffers and the addition of lime-water increases the concentration of the hydroxyl-ions, which combine with the hydrogen-ions, forming water; in the case of the soils with a large amount of organic substance, the amount of buffer is much larger and thus prevents the suppression of the hydrogen ions.

The amount of buffer in soils with an abundance of plant residues will differ with each soil; the slightest change in the organic substances will produce a different amount of complex organic compounds with different degrees of buffer action; the amount of buffer can be measured when the hydroxylions reach a point where the buffer has no more effect and the curve begins to rise gradually; this point is the end-point of the buffer action. The curves of samples 14, 20 and 21 illustrate the effect of buffers.

It seems to the author that in the case of sandy soil with little organic matter, an adjustment of the reaction to neutrality, or any point desired, may be accomlished very conveniently by the hydrogen-ion concentration method in a very short time, avoiding the tedious procedure of the Veitch method The curves of samples 13, 15, 18, 23 and 24 show the possibilities of adjusting the soil reaction in sandy soils. It is of interest to note the relation of the curves of samples 21, 22, 23 and 24.   They are from the same soil of different depths, as pointed out in table 1.   It is characteristic that the surface soil with the plant residues has an irregular curve, and as we approach the lower depths the tendency of the curve is to become regular.   The same kind of a curve would be produced by samples 8, 9, 10 and 11.   Looking over the pH
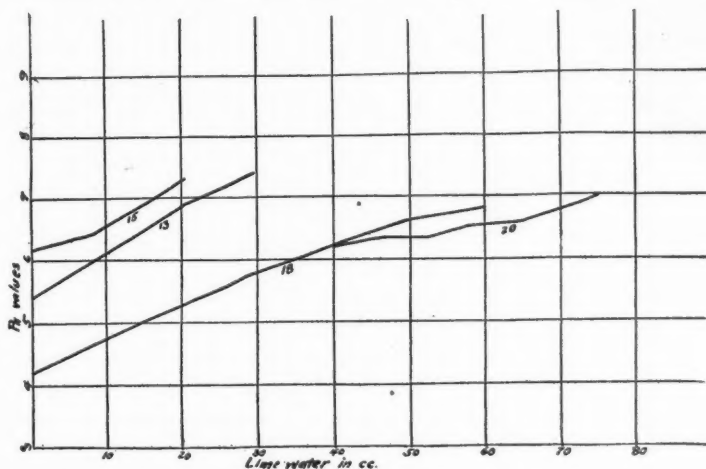

Fig. 2. Curves of Hydrogen-Ion Concentration of Samples 13, 15, 18 and 20

values before and after evaporation, we notice that if we get a pH value between 6.6 and 6.8 before evaporation we are certain that we have reached the point of the "lime requirement."   By such a procedure we may save more than half the time which the evaporations in the Veitch method take.

As was stated in the earlier part of this article, this is not a study of the hydrogen-ion concentration measurements of soils.   Incidentally, it points toward a method for the determination and adjustment of the soil reaction in sandy soils and possibly even in soils with a high organic-matter content. The author feels that more elaborate experimentation in this line is essential, in order to establish the proposed scheme.

The author takes this opportunity to thank Dr. Selman A. Waksman for reading the manuscript and offering helpful criticism.

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THE RELATIVE ABSORPTION BY SOIL OF SODIUM CARBONATE AND SODIUM CHLORIDE

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A number of papers have been published recently which describe investigations of the effect upon plant growth of "alkali" salts when added to the soil and in which conclusions as to the relative toxicity of the different salts are based upon the quantity of salt added (5, 7, 12).[1] The disadvantage of this method of interpreting the results is that it does not take into account differences in the proportion of the solute which is withdrawn from the solution when different salts are brought into contact with a soil. This source of error was noted several years ago by Mr. W. H. Heileman, formerly of the Bureau of Soils, United States Department of Agriculture, in the course of experiments with seedling plants grown in soils to which salts of sodium had been added. He observed that under these conditions sodium carbonate appeared to be much less toxic in comparison with sodium chloride than had been indicated by numerous observations upon plants growing in natural alkali soils and by the results of water culture experiments.[2]

It has been shown by Headley, Curtis and Scofield (8) that when sodium carbonate is added to a soil, upon analysis of the soil extract after several weeks, the quantity recovered is much less than the quantity which had been added, even when allowance is made for the increase in the content of bicarbonates which has taken place. In the case of sand, to which had been added solutions of sodium carbonate in eight concentrations ranging from 0.05 to 0.40 per cent, the quantity recovered of sodium carbonate plus excess of sodium bicarbonate reckoned as carbonate averaged 69.0 ± 2.9 per cent. In the case of a loam soil to which had been added solution of sodium carbonate in 10 concentrations ranging from 0.05 to 0.60 per cent, the quantity recovered averaged only 26.0 ± 1.7 per cent.[3] In other words the sand had

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[1] The readiness with which sodium carbonate is absorbed, and the necessity of considering this factor in relation to the toxicity of soils to which this salt has been added, are recognized in other publications by Harris and Pittman (6, 11).

[2] Thus Kearney and Cameron (9, p. 19, 24, 33, 36) found that both in pure solution and in the presence of an excess of calcium carbonate and of calcium sulfate, sodium carbonate was much more toxic to the roots of white lupine than was sodium chloride. Similar results with various crop plants were obtained by Kearney and Harter (10).

[3] These percentages have been computed from data given in table 3, p. 863 of the publication cited.

absorbed 31 per cent and the loam had absorbed 74 per cent of the sodium carbonate which had been added to the soil.

Very different results with sodium chloride were obtained by the same investigators. This salt was added to a loam soil in six concentrations of solution ranging from 0.05 to 0.60 per cent and when the soil extract was analyzed several weeks later the quantity of sodium chloride recovered averaged 84.0 ± 1.5 per cent.[4] In a parallel experiment with the same soil to which had been added sodium carbonate solutions in eight concentrations ranging from 0.05 to 0.40 per cent, the quantity recovered of sodium carbonate, plus excess sodium bicarbonate reckoned as the carbonate, averaged only 23.5 ± 2.3 per cent.[5] In other words, the loam soil had absorbed 76.5 per cent of the sodium carbonate and only 16 per cent of the sodium chloride which had been added.

A further source of error, in experiments dealing with the relative toxicity of sodium carbonate, when conclusions are based solely upon the quantity of salt which has been added to the soil, lies in leaving out of account the reaction which takes place with carbon dioxide, resulting in the formation of the bicarbonate at the expense of the normal carbonate. It was demonstrated by Cameron and Briggs (3) that in solutions of sodium carbonate at a temperature of 25°C. and in concentrations ranging from 0.2 to 0.6 per cent, approximately half of the normal carbonate is replaced by the bicarbonate. In the above cited publication by Headley, Curtis and Scofield, evidence is given that a similar reaction occurs when sodium carbonate is added to soil, a large proportion of the salt being recovered in the form of bicarbonate. Sodium bicarbonate is less toxic than the normal carbonate, as was shown by the results of an experiment performed by Kearney and Cameron (9, p. 19 and 20; see also ref. 10) in which roots of the white lupine were exposed to solutions of sodium bicarbonate wherein the formation of the normal carbonate was prevented by the presence of an excess of carbon dioxide. Therefore when sodium carbonate is added to a soil, not only is the total concentration of the soil solution much smaller than would be assumed from the quantity of salt added, but much of the salt which remains in the soil solution is in the form of the less toxic bicarbonate.[6]

RELATIVE ABSORPTION AS INDICATED BY ELECTRICAL RESISTANCE

A comparison of different salts of sodium in respect to the relative degree of absorption in a soil, as measured by the electrical resistance of the system, was made by Davis and Bryan (4), who, however, apparently made their

[4] As computed from data given in table 5, p. 867.

[5] As computed from data given in table 2, p. 861.

[6] It might be thought that owing to the unstable equilibrium between the carbonate and bicarbonate, the relative toxicity of the two salts is of no practical importance. As a matter of fact, however, bicarbonates are sometimes present in large quantity in soils which do not give the hydroxyl reaction with phenolphthalein.

readings immediately after the solutions were added to the soil. In order to test adequately the usefulness of the electrical resistance method for determining differences in absorption of different salts by a soil, more time should be allowed for the system to reach an equilibrium. This has been done in an experiment performed by the writer, which is described below.

Solutions of sodium chloride and sodium carbonate, of concentrations ranging from 0.05 to 1.00 per cent, were added to air-dry sand in sufficient quantity to supersaturate it slightly.

The sand used had a moisture equivalent[7] of 2.4 per cent, indicating a moisture-holding capacity of 25 per cent and the quantity of solution added was 26 per cent of the dry weight of the sand. This sand was relatively free from readily soluble material, as is indicated by the fact that when saturated

TABLE 1

Electrical resistances at 60°F. of the free solutions when the cup is filled to 40 per cent and to 100 per cent of its capacity (20 cc. and 50 cc., respectively)

CONCENTRATION OF SOLUTION	SODIUM CARBONATE			SODIUM CHLORIDE		
	Resistance of solution		Ratio of resistance of 20 cc. to that of 50 cc.	Resistance of solution		Ratio of resistance of 20 cc. to that of 50 cc.
	20 cc.	50 cc.		20 cc.	50 cc.	
per cent	*ohms*	*ohms*		*ohms*	*ohms*	
1.00	63	22	2.86	53	19	2.79
0.80	75	28	2.68	65	24	2.71
0.60	98	34	2.88	89	32	2.78
0.40	135	49	2.75	126	46	2.74
0.20	246	90	2.73	240	85	2.82
0.10	500	167	2.99	467	171	2.73
0.05	872	328	2.65	872	323	2.70
	Average ratio 2.79 ± 0.03			Average ratio 2.75 ± 0.01		

with distilled water and allowed to stand 24 hours, its electrical resistance was about 2500 ohms. When the sand was moistened with the solution the mixture was thoroughly stirred and was allowed to stand for 24 hours, when it was again stirred. The cup of the electric bridge was then filled with the wet sand and the electrical resistance of the latter was determined and was corrected to a temperature of 60°F.

The electrical resistances of the different concentrations of the free solution of each salt also were determined, both with the bridge cup full (50 cc.) and with only 20 cc. of solution in the cup, the latter corresponding to the moisture content of the cup when filled with the wet sand.

The resistances of 20 cc. and of 50 cc. of each concentration of solution of the two salts are stated in table 1, which also gives for each concentration the

[7] As determined by the centrifugal method (1). A formula for computing the moisture-holding capacity from the moisture equivalent is given by Briggs and Shantz (2).

ratio of the two resistances. It is evident that, for the range of concen-
trations used, this ratio is practically a constant. It is also evident that with
an equal concentration and volume of solution the resistances of the two
salts differ only slightly.

In table 2 are given, for each concentration of each salt, the resistance of
the saturated sand (containing 20 cc. of the solution), the resistance of 20 cc.
of the free solution and the ratio of the first to the second resistance. The
ratios are graphically expressed in figure 1.

If the presence of the sand had had no effect upon the resistance of the
solution in contact with it, the ratio of the two resistances for each con-
centration of each salt should have been 1.0, since the quantity and the
original concentration of solution were the same in both cases. The degree

TABLE 2

*Resistances at 60°F. of the saturated sand (cup full) and of 20 cc. of the corresponding
free solution*

CONCENTRATION OF SOLUTION	SODIUM CARBONATE			SODIUM CHLORIDE		
	Resistance of		Ratio of re-sistance of sand to solution	Resistance of		Ratio of re-sistance of sand to solution
	Saturated sand	Solution (20 cc.)		Saturated sand	Solution (20 cc.)	
per cent	*ohms*	*ohms*		*ohms*	*ohms*	
1.00	146	63	2.3	77	53	1.5
0.80	198	75	2.6	90	65	1.4
0.60	234	98	2.4	116	89	1.3
0.40	416	135	3.1	180	126	1.4
0.20	765	246	3.1	317	240	1.3
0.10	1159	500	2.3	594	467	1.3
0.05	1539	872	1.8	1014	872	1.2
0	2488*			2488*		
	Average ratio 2.5 ± 0.12			Average ratio 1.3 ± 0.02		

* Control, sand saturated with distilled water.

to which the ratio exceeds unity therefore indicates the degree to which the
resistance of the solution in contact with the sand has been increased by
withdrawal of a portion of the solute. It is evident that in the case of
sodium carbonate much more of the solute has been withdrawn than in the
case of sodium chloride, the dilution due to contact with the sand having in-
creased the resistance, for the several concentrations, nearly twice as much in
the former case as in the latter.

A glance at figure 1 shows that the curves representing the ratios of the two
resistances differ greatly for the two salts, that for sodium chloride being
much flatter than the curve for sodium carbonate, which shows a con-
spicuous maximum at concentrations of 0.20 and 0.40 per cent. Discussion
of this difference, the significance of which could be ascertained only by

repeated determinations, is beside the purpose of the present article, since the data given sufficiently answer the question whether sodium carbonate is withdrawn from solution in greater proportion than sodium chloride, when in contact with soil.

It should be noted that the resistances of sand saturated with solutions of corresponding concentration of sodium carbonate and of sodium chloride, as given in the publication of Davis and Bryan (4, p. 13, table 1), are much
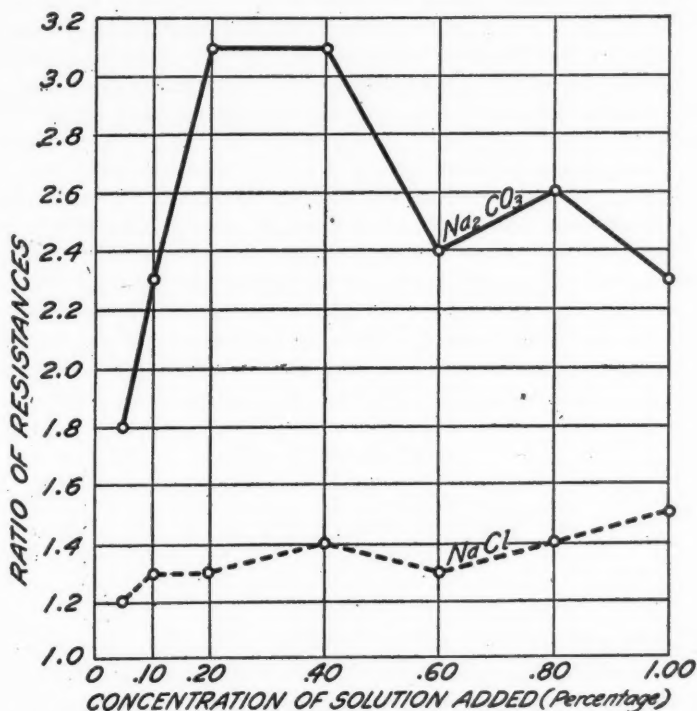

FIG. 1.   RATIO OF RESISTANCE OF SAND PLUS 20 CC. OF SOLUTION TO THAT OF 20 CC. OF FREE SOLUTION

lower than the resistances in sand obtained by the writer, and also show little difference as between the two salts.   The probable explanation is that Davis and Bryan determined the resistance immediately after adding the solution to the soil, while in the writer's experiment the readings were made after solution and soil had remained in contact during 24 hours.

Inspection of table 2 shows that when this amount of time is allowed, sand to which sodium carbonate has been added at concentrations of 0.10 to 1.00 per cent, gives a resistance about double that of sand to which like con-

centrations of sodium chloride have been added.   Roughly speaking, the soil
solution in the latter case is about twice as concentrated as in the former, yet
if unaware of how differently the two salts are absorbed by the sand, one
might assume that the soil solutions, like the original solutions, were of equal
concentration in both cases.

In order to obtain some idea of the actual concentration, of the solution
present in the sand to which sodium carbonate had been added 24 hours
previously, a curve was plotted for the electrical resistances of 20 cc. of the
free solution at the several concentrations which had been added.   The curve
was extended so as to include resistances as high as those of the sand to which
the two most dilute solutions had been added, by determining the resistances
of 20 cc. each of 0.04 per cent and 0.03 per cent sodium carbonate in free solu-
tion, the resistances obtained for these concentrations having been 1120 and
1580 ohms, respectively.   By reading on the curve the concentration corre-
sponding to the electrical resistance of the saturated sand, an approximate idea
was obtained of the concentration of the solution present in the latter.   For
the 6 concentrations 0.10 to 1.00 per cent, the concentration of the solution
present in the sand as thus estimated averaged 37 per cent (range 34 to 40
per cent) of that which had been added, indicating that approximately 63
per cent of the salt had been withdrawn from the solution when in contact
with the sand.   A similar calculation in the case of sodium chloride indicated
an average absorption of only 23 per cent of the salt which had been added.

CONCLUSIONS

When equal volumes of solution of equal concentration of sodium carbonate
and of sodium chloride are added to sand and the solution and soil are allowed
to remain in contact during several hours, the electrical resistance of the
sand to which sodium carbonate has been added is much higher than that
of the sand to which sodium chloride has been added.

Since the greater resistance in the case of sodium carbonate must be due to
proportionately greater withdrawal of the solute by the sand, it follows that
plants growing in soils to which equal quantities of the two salts have been
added are in contact with soil solutions of very unequal concentration.

As a result of overlooking this factor, as well as the reaction which takes
place in solutions of sodium carbonate resulting in the formation of the less
harmful bicarbonate, certain investigators of the effects of "alkali" salts upon
plant growth have concluded that sodium carbonate is less toxic than sodium
chloride.   Observations upon plants growing in natural alkali soils and ex-
periments with seedlings exposed to pure solutions of these salts have shown
the contrary to be true.

The results of the experiment described in this paper indicate that the
electrical bridge affords a convenient means for determining the degree to
which different salts are withdrawn from a solution which has been added to

a soil. In the case of sodium carbonate and sodium chloride, equivalent solutions of which (at the concentrations ordinarily encountered in alkali soils) do not differ greatly in electrical resistance, the bridge method permits direct comparison of the concentration of the solution in soils to which these salts have been added.

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